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Characterizing the gas-phase reactivity of multigenerational air pollutants

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Abstract

The reactive intermediates being formed during multigenerational oxidation processes remain a poorly understood aspect of atmospheric chemistry. These species play crucial roles in atmospheric transformations, many of which are closely implicated in the formation of secondary organic aerosols or in serving as indirect sources of potent greenhouse gases. Understanding the kinetics of multigenerational oxidation products is therefore essential for accurately assessing the impacts of anthropogenic and biogenic emissions on air quality and climate.

This thesis aims to make progress on current key scientific issues through laboratory experiment and methodological innovation. From the perspective of anthropogenic emissions, a major focus has been placed on synthetic fluorinated gases widely used in the industry, which have recently been implicated in the indirect production of the potent greenhouse gas CHF_3 through the photolysis of their key degradation intermediate, trifluoroacetaldehyde. This thesis provides a quantitative assessment on this unaccounted-for atmospheric source of CHF_3 through a series of photolysis experiments, and systematically evaluates the contribution of this secondary chemistry to the indirect global warming potential (GWP) increase of its fluorinated precursors. From the perspective of biogenic emissions, attention was directed to chemistry of Criegee intermediates (CIs). Despite being a ubiquitous product of alkene ozonolysis and despite their high reactivity in the atmosphere, their kinetic data have long remained sparse. Accordingly, we developed and validated a chamber-based relative rate approach for measuring CI kinetics, and applied it to insertion reactions with a selection of acids and alcohols. This method offers multiple advantages (e.g., for experimenting on low-volatility co-reactants) and is expected to be applied to more determination for CI bimolecular reactions, complementing existing absolute techniques. Based on the insertion mechanism of CIs with acids, we further achieved the gas-phase synthesis of α -alkoxyacyl hydroperoxides (ROOHs) and explored their reactivities toward OH, NO_3 , and CIs. The kinetic data obtained provide a context for evaluating the atmospheric lifetimes and competing removal pathways of these simple functionalized ROOHs for the first time, thereby offering insights for understanding more complex multifunctional hydroperoxides and their potential contribution to secondary organic aerosol formation.

Résumé

Les intermédiaires de réactions formés au cours des processus d'oxydations multigénérationnelles demeurent un aspect encore mal compris de la chimie atmosphérique. Ces espèces jouent un rôle crucial dans les transformations atmosphériques, beaucoup étant étroitement impliquées dans la formation d'aérosols organiques secondaires ou constituent des sources indirectes de gaz à effet de serre puissants. La compréhension de la cinétique de ces produits d'oxydation est donc essentielle pour évaluer avec précision les impacts des émissions anthropiques et biogéniques sur la qualité de l'air et sur le climat.

Cette thèse vise à faire progresser plusieurs questions scientifiques clés actuelles à travers des expériences en laboratoire et des innovations méthodologiques. Concernant les émissions anthropiques, l'accent a été mis sur les gaz fluorés de synthèse largement utilisés dans l'industrie et qui ont récemment été impliqués dans la production indirecte du puissant gaz à effet de serre CHF_3 par la photolyse de leur principal intermédiaire de dégradation, le trifluoroacétaldéhyde. Cette thèse présente une étude quantitative de cette source atmosphérique non répertoriée de CHF_3 à partir d'une série d'expériences de photolyse, et évalue la contribution de cette chimie secondaire à l'augmentation indirecte du potentiel de réchauffement global de ses précurseurs fluorés. Du point de vue des émissions biogéniques, l'attention a été portée sur la chimie des intermédiaires de Criegee (CI). Bien qu'ils constituent un produit systématique de l'ozonolyse des alcènes et qu'ils soient hautement réactifs dans l'atmosphère, leurs données cinétiques demeuraient longtemps limitées. Par conséquent, nous avons développé et validé une méthode des vitesses relatives en chambre pour mesurer la cinétique des CI, et l'avons appliquée à des réactions d'insertion avec une sélection d'acides et d'alcools. Cette approche présente de multiples avantages, par exemple pour l'étude de co-réactifs peu volatils, et devrait permettre d'obtenir davantage de données concernant les réactions bimoléculaires des CI, en complément des techniques absolues existantes. Sur la base du mécanisme d'insertion des CI avec les acides, nous avons également synthétisé en phase gazeuse des α -alkoxyacyl hydroperoxydes (ROOHs) et exploré leur réactivité vis-à-vis de OH, NO_3 et des CI. Les données cinétiques obtenues permettent d'évaluer, pour la première fois, les durées de vie atmosphériques et les voies d'élimination concurrentes des ROOHs simplement substitués, apportant ainsi des éléments de compréhension sur les hydroperoxydes multifonctionnels plus complexes et leur contribution potentielle à la formation d'aérosols organiques secondaires.

Résumé général

La présente thèse porte sur les processus chimiques atmosphériques en phase gazeuse, avec un accent particulier sur l'évolution multigénérationnelle des composés organiques dans l'atmosphère. Le manuscrit de thèse est constitué de cinq chapitres. Le Chapitre 1 présente une introduction générale, dans lequel les diverses sources et voies d'élimination des constituants atmosphériques sont décrites, tout en posant les bases conceptuelles de la chimie atmosphérique. Le Chapitre 2 explore un effet de réchauffement climatique résultant de la dégradation atmosphérique, en examinant la photolyse du trifluoroacétaldéhyde sous des longueurs d'onde pertinentes pour l'atmosphère et son potentiel de formation de HFC-23, un puissant gaz à effet de serre. Le Chapitre 3 développe une technique cinétique relative, basée sur l'utilisation d'une chambre de simulation atmosphérique, pour étudier la chimie des intermédiaires de Criegee stabilisés, améliorant ainsi notre capacité à évaluer la réactivité de ces espèces clés issues de l'ozonolyse des alcènes. Le Chapitre 4 examine l'oxydation en phase gazeuse des hydroperoxydes synthétisés in situ via un système d'ozonolyse en chambre de simulation de grand volume. Ces hydroperoxydes représentent des produits de fin de chaîne, hautement multifonctionnels, dotés d'un fort potentiel de formation d'aérosols organiques secondaires. Le Chapitre 5 résume les principaux résultats de cette thèse et propose des perspectives de recherche future.

Chapitre 1 : Introduction à la chimie atmosphérique

La chimie atmosphérique est la science dont l'objectif est de comprendre comment les espèces traces réactives se forment, se transforment, et comment leurs réactions influencent la qualité de l'air, le climat et la santé humaine. Au cœur des transformations atmosphériques se trouvent les cinétiques de réactions, c'est-à-dire l'étude des vitesses à laquelle les réactions chimiques se produisent et dans quelles conditions, fournissant ainsi le lien essentiel entre la réactivité chimique à l'échelle moléculaire et les conséquences à l'échelle globale. Savoir si une réaction se produit en quelques millisecondes ou en plusieurs centaines d'années détermine si un polluant persiste, où il est transporté, et ce qu'il devient en fin de compte. Les études cinétiques permettent de quantifier les constantes de vitesse des réactions, les dépendances à la pression et à la température, autant de paramètres essentiels à l'élaboration de modèles chimiques atmosphériques prédictifs et fiables. En parallèle, la compréhension des mécanismes chimiques sous-jacents et l'identification des produits sont indispensables pour évaluer l'importance relative des voies réactionnelles en compétition et leurs implications sur la composition de l'atmosphère et le climat.

Dès les années 1950, les scientifiques ont découvert que l'interaction entre le rayonnement solaire et les composés organiques volatils (COV), les oxydes d'azote (NO_x) et le dioxyde de soufre (SO_2) déclenchait une série de réactions photochimiques menant à la formation de smog. Aujourd'hui, la pollution de l'air reste l'un des dix principaux risques sanitaires mondiaux, causant chaque année des millions de décès prématurés.

Les substances chimiques impliquées dans les épisodes de pollution proviennent d'un large éventail de sources. Celles-ci peuvent être naturelles : forêts, océans, feux de forêts, volcans, déserts ; mais aussi d'origine anthropique : agriculture, industries, combustion de combustibles fossiles et de biomasse, etc. La pollution atmosphérique est étroitement liée au changement climatique, car certains polluants émis dans l'air, comme le dioxyde de carbone (CO_2), le méthane, le protoxyde d'azote et les gaz fluorés (F-gaz), sont également des gaz à effet de serre.

Au cœur de cette chimie se trouvent les oxydants atmosphériques, tels que les radicaux hydroxyle (OH) et nitrate (NO_3), l'ozone (O_3) et les atomes de chlore (Cl). Ces oxydants gouvernent la transformation atmosphérique des polluants traces par des chaînes réactionnelles complexes d'initiation, de propagation et de terminaison radicalaire. Il est essentiel de souligner que, lorsqu'ils sont émis dans l'atmosphère, les composés organiques volatils (COV) ne subissent pas une dégradation linéaire et unique. Chaque molécule traverse au contraire une série de voies réactionnelles concurrentes avant d'être éliminée. La trajectoire exacte suivie par une molécule et l'identité de ses produits dépendent fortement de sa structure chimique ainsi que de la sélectivité des oxydants atmosphériques envers différents sites réactifs. Ce partage compétitif entre multiples voies de dégradation contribue de manière significative à la complexité croissante de la composition organique atmosphérique. Par exemple, pour un composé comme l' α -pinène ($\text{C}_{10}\text{H}_{16}$), le nombre de produits moléculaires distincts formés en seulement quelques générations d'oxydation peut être considérable. Des estimations suggèrent que l' α -pinène à lui seul peut générer plus de 500 000 structures chimiques uniques via les processus chimiques atmosphériques.

Au-delà du simple nombre de produits d'oxydation, une autre dimension essentielle de la dégradation atmosphérique réside dans les comportements physico-chimiques et les interactions environnementales des produits formés. De nombreux intermédiaires issus de la dégradation atmosphérique lors des processus d'oxydation multigénérationnelle ne sont pas nécessairement moins nocifs que leurs composés précurseurs. Au contraire, ils peuvent présenter une persistance et une toxicité accrues, contribuer à la formation d'aérosols organiques secondaires en raison de leur faible volatilité et de leur multifonctionnalité, ou encore agir comme des gaz à effet de serre plus puissants que les composés issus des émissions d'origine.

Chapitre 2 : Photolyse du CF_3CHO comme source potentielle de CHF_3 – un exemple représentatif de l'effet de réchauffement climatique lié aux émissions anthropiques

Un exemple marquant des processus d'oxydation multigénérationnelle est la dégradation atmosphérique des gaz fluorés mentionnés précédemment, qui sont largement utilisés dans divers secteurs industriels (par exemple, comme réfrigérants, solvants et agents de gonflement pour mousses) depuis leur introduction dans les années 1930. Les préoccupations relatives à l'appauvrissement de la couche d'ozone et au changement climatique ont conduit à une série d'interdictions réglementaires progressives : d'abord les chlorofluorocarbures (CFC), puis les hydrochlorofluorocarbures (HCFC), et enfin la réduction en cours des hydrofluorocarbures (HFC). Les familles de composés du type hydrofluoro-oléfines (HFO) et les hydrochlorofluoro-oléfines (HCFO) ont émergé comme des alternatives de nouvelle génération, présentant un faible potentiel d'appauvrissement de l'ozone (ODP) et un potentiel de réchauffement global (PRG) direct quasi nul, principalement en raison de leur forte réactivité vis-à-vis des oxydants atmosphériques, de leur durée de vie atmosphérique courte et de l'absence des atomes de chlore et brome.

Les HFO et HCFO se décomposent facilement dans l'atmosphère pour former des carbonyles fluorés, comme le trifluoroacétaldéhyde (CF_3CHO), un composé photolabile. Le CF_3CHO est un produit de dégradation courant, formé en rendements élevés lors de la transformation atmosphérique initiée par les radicaux OH des gaz fluorés contenant un groupement « CF_3CH_2- » ou « $\text{CF}_3\text{CH=}$ ».

Une question de longue date, cruciale pour la transition vers des gaz industriels sûrs, est de savoir si la décomposition atmosphérique du CF_3CHO conduit à la formation de CHF_3 (fluoroforme, HFC-23), un des puissants gaz à effet de serre, avec une durée de vie atmosphérique de 228 ans et un potentiel de réchauffement global (PRG) de 14,700 sur un horizon de 100 ans. Il est important de noter que les émissions mondiales de HFC-23 restent mal quantifiées, avec un écart estimé de 13,9 kilotonnes par an en 2020 entre les valeurs observées et déclarées par les états. Cette incertitude a soulevé des inquiétudes quant à l'existence de sources atmosphériques non prises en compte dans la production de HFC-23.

Le CF_3CHO , comme la plupart des composés carbonylés, peut réagir avec les radicaux OH ou subir une photolyse suite à l'absorption du proche ultraviolet via le chromophore CHO. La fluoration du groupe méthyle renforce la liaison C–H, et la constante de vitesse de réaction avec les radicaux OH, $k_{\text{OH}} = 5,7 \times 10^{-13} \text{ cm}^3 \text{ molécule}^{-1} \text{ s}^{-1}$, est bien inférieure à celle des aldéhydes alkylés substitués, ce qui fait de la photolyse la principale voie d'élimination atmosphérique. La photodissociation du CF_3CHO suit trois voies principales :



Afin d'évaluer de manière approfondie la photolyse atmosphérique du CF_3CHO et son potentiel de production de CHF_3 , nous avons mené une série d'expériences en laboratoire sous différentes conditions d'irradiation UV, en utilisant notamment un réacteur tubulaire spécialement conçu (LARKIN) et la chambre de simulation atmosphérique (HELIOS). L'objectif était de quantifier à la fois les rendements quantiques de la photodégradation du CF_3CHO (Φ_{total}) et les rendements de formation du CHF_3 (Φ_{CHF_3}) en fonction de la longueur d'onde, avec un accent particulier sur la région actinique. Le CF_3CHO a été synthétisé et purifié au laboratoire. Le photoréacteur LARKIN (Long-Axis Reactor for KINetic) a été conçu spécialement pour cette étude, avec une source lumineuse accordable. Dans le système LARKIN, la photolyse UV monochromatique a été réalisée avec une détection in situ par spectroscopie infrarouge à transformée de Fourier (IRTF) et un système SPIRIT (Spectromètre Infrarouge In situ Troposphérique) très sensible, permettant la détection du CHF_3 à l'échelle du ppb. Les interférences croisées du CF_3CHO ont été soigneusement corrigées, et le système SPIRIT a été rigoureusement calibré à l'aide d'un gaz étalon de CHF_3 , également préparé en interne avec plusieurs répliques pour garantir la précision et reproductibilité de nos mesures. La chimie radicalaire secondaire a été contrôlée dans les expériences, où l' O_2 capte efficacement les radicaux CF_3 ou CF_3CO et met fin aux chaînes radicalaires en favorisant la formation de CF_2O , tandis que le CO piège efficacement les radicaux OH et CF_3O , empêchant les réactions secondaires et les pertes non souhaitées de CF_3CHO . Afin de minimiser les interférences chimiques et les erreurs systématiques, les rendements quantiques du CF_3CHO et les rendements en produit CHF_3 ont été déterminés de manière indépendante dans des expériences séparées. Les rendements quantiques absolus de photolyse ont été déterminés par comparaison avec un composé de référence bien établi à différentes longueurs d'onde (248, 290, 300, 310, 315 et 320 nm). Les rendements en CHF_3 ont été mesurés séparément à 248, 290, 300, 305 et 310 nm en utilisant SPIRIT comme méthode de détection principale, sous différentes concentrations initiales de CF_3CHO . Une grande précision et de bonnes linéarité et reproductibilité ont été observées entre les expériences dans chaque cas. Un accord raisonnable avec les mesures précédentes reportées dans la littérature a été observé aux courtes longueurs d'onde, tandis que des divergences plus importantes existent pour les rendements en CHF_3 dans la région actinique.

Des expériences complémentaires de photolyse UV à large bande ont été menées sous irradiation naturelle et artificielle dans la grande chambre de simulation en téflon (HELIOS). Sous irradiation par le rayonnement solaire naturel, aucune perte photolytique mesurable de CF_3CHO n'a été observée ; même sous une irradiation UV artificielle intensifiée, la production de CHF_3 restait inférieure au seuil de détection, bien qu'une légère dégradation photolytique de CF_3CHO ait été détectée. Cela souligne l'utilité limitée des grandes chambres de simulation atmosphériques pour détecter les produits à faible rendement, sauf dans le cas d'utilisation de concentrations de précurseurs trop élevées comparées aux conditions atmosphériques réalistes. À cet égard, le réacteur LARKIN, de petit volume et doté d'une source lumineuse accordable, constitue une méthode plus adéquate, pratique et sensible.

Pour mieux comprendre la pertinence atmosphérique de la formation de CHF_3 , nous avons évalué l'importance des trois principales voies de dégradation de CF_3CHO par photolyse, oxydation par OH et oxydation par HO_2 tout au long de la colonne atmosphérique verticale. Les résultats ont montré que la photolyse, dépendante de la pression, domine l'élimination du CF_3CHO à toutes les altitudes, avec des durées de vie plus courtes aux altitudes plus élevées en raison de l'augmentation du flux de photons UV et de la baisse de la pression. Les rendements en CHF_3 restent très faibles ($\sim 0,002\text{--}0,006\%$) dans toute la troposphère mais deviennent relativement significatifs ($>0,1\%$) au-dessus d'environ 30 km.

Comme mentionné ci-dessus, le CF_3CHO est un intermédiaire commun dans la dégradation de nombreux gaz fluorés ; sa capacité à générer CHF_3 est étroitement liée aux lieux d'émission du CF_3CHO lui-même ou de ses précurseurs, ainsi qu'à leur capacité à être transportés dans la haute atmosphère. Nous avons comparé dans cette étude la distribution verticale de plusieurs composés fluorés représentatifs, notamment les hydrofluorooléfines (HFO), les hydrofluoroéthers (HFE), les hydrochlorofluorocarbures (HCFC), les halons et les hydrofluorocarbures (HFC), en fonction de leur réactivité avec les radicaux OH. Les résultats indiquent que les HFO se dégradent rapidement dans la troposphère et contribuent donc peu à la formation de CHF_3 . En revanche, certains HFE, HCFC, halons et en particulier HFC à longue durée de vie atteignent la stratosphère, où la formation de CF_3CHO et donc la production de CHF_3 deviennent plus favorables.

En résumé, nous avons caractérisé la photolyse du CF_3CHO à 248 nm et dans toute la région actinique. Nous constatons qu'il peut être une source de CHF_3 , bien que les rendements en produit soient faibles. En tant que précurseurs du CF_3CHO , la nature à courte durée de vie des HFO se traduit par un faible potentiel de réchauffement climatique indirect, tandis que les précurseurs à plus longue durée de vie comme les HFC nécessitent une attention accrue. À l'avenir, alors que les émissions de composés

fluorés continuent d'augmenter et que des structures de molécules fluorées plus complexes pourraient être introduites, une surveillance continue des voies de dégradation et des sous-produits sera essentielle. Nos résultats soulignent l'importance de caractériser avec précision les durées de vie atmosphériques et les produits de dégradation afin de garantir que la prochaine génération de réfrigérants et de solvants industriels remplisse véritablement ses promesses en matière de climat et d'environnement.

Chapitre 3 : Cinétique des intermédiaires de Criegee – un oxydant important mais encore peu étudié, issu de précurseurs biogéniques

Les émissions de composés organiques volatils biogéniques (COVB) dépassent largement les émissions anthropiques à l'échelle globale, avec des émissions d'isoprène à elles seules estimées entre 500 et 750 Tg par an. Une caractéristique commune à bon nombre de ces COVB est leur insaturation (par exemple, l'isoprène et les nombreuses molécules terpénoïdes). En raison de la présence de doubles liaisons oléfiniques, ces alcènes peuvent rapidement réagir avec l'ozone dès leur entrée dans l'atmosphère, ce qui conduit à la formation d'un ozonide primaire cyclique et énergisé, lequel se décompose rapidement en un composé carbonylé et un oxyde carbonylé, plus communément appelé intermédiaire de Criegee (CI). Au cours de l'étape initiale de la réaction, une partie des CI est produite avec un excès d'énergie interne, subissant alors des réarrangements unimoléculaires rapides qui donnent lieu à une cascade de produits stables et des radicaux libres. Toutefois, dans des conditions atmosphériques, une fraction des CI est stabilisée par collisions avec des molécules inertes, formant ainsi des intermédiaires de Criegee stabilisés (SCI). Contrairement à leurs homologues excités, les SCI ont des durées de vie atmosphériques plus longues et peuvent participer à une variété de réactions bimoléculaires : insertion (par exemple avec l'eau, les alcools ou les hydroperoxydes), addition (par exemple avec le NO₂ ou les radicaux peroxy) et cycloaddition (par exemple avec le SO₂, les alcènes ou les carbonyles). Ces réactions conduisent à la formation de produits hautement fonctionnalisés, de polarité accrue et de volatilité réduite, pouvant contribuer de manière significative à la formation d'aérosols organiques secondaires (SOA) dans l'atmosphère.

L'identité d'un CI est déterminée par les substituants présents sur l'alcène précurseur dans la réaction d'ozonolyse. En raison de son caractère zwitterionique, il peut exister sous plusieurs conformères séparés par des barrières rotationnelles significatives. Ainsi, par exemple, l'ozonolyse de l'isoprène peut donner lieu à neuf intermédiaires de Criegee distincts. Il en découle que la diversité des CI présents dans l'atmosphère pourrait surpasser celle des alcènes eux-mêmes. En outre, en raison de la diversité des voies réactives accessibles aux CI, le champ des co-réactifs atmosphériques potentiels est extrêmement vaste. Toute molécule possédant une liaison hydrogénée labile peut être cible d'une

réaction d'insertion, tandis que les espèces présentant des liaisons insaturées sont susceptibles de subir une cycloaddition. Il en résulte un espace paramétrique très vaste pour la cinétique des réactions bimoléculaires des SCI, dont seule une petite fraction a été caractérisée expérimentalement à ce jour.

Un obstacle majeur réside dans le nombre limité de méthodes expérimentales fiables permettant d'étudier ces réactions. Les techniques absolues de mesure de constantes de vitesse, bien que précises, reposent souvent sur des précurseurs photolytiques comme les gem-diiodoalcane. Or, ces composés sont non seulement difficiles à synthétiser et rarement disponibles dans le commerce, mais présentent également de faibles pressions de vapeur, ce qui limite leur utilisation, en particulier avec des réactifs peu volatils ou multifonctionnels. De plus, les mesures absolues exigent généralement des conditions pseudo-premier ordre, impliquant un large excès de co-réactifs. Cela empêche l'étude de composés à faible volatilité qui pourraient pourtant être d'une grande importance atmosphérique. D'autres biais systématiques, tels que les réactions secondaires impliquant des espèces iodées, l'auto-réactivité des SCI ou le chevauchement des spectres UV, peuvent également nuire à la fiabilité des résultats. Ces contraintes laissent aujourd'hui une base de données cinétiques largement incomplète, où seules quelques combinaisons SCI-réactif ont pu être quantifiées expérimentalement.

Dans ce chapitre, nous visons à surmonter ces limitations en développant une méthode relative de mesure des constantes de vitesse dans une chambre de simulation atmosphérique. Les expériences ont été menées dans HELIOS, la plus grande chambre de simulation atmosphérique extérieure en France, d'un volume de 90 m³. Un élément clé de notre conception expérimentale consiste à utiliser des alcènes hautement symétriques afin d'assurer la formation d'un seul type de SCI par ozonolyse classique ; ainsi, l'éthylène, le plus simple des alcènes, a été choisi dans cette étude de principe pour produire exclusivement l'oxyde de formaldéhyde, CH₂OO. Afin de garantir que le réactif cible et le composé de référence réagissent uniquement avec ce même oxydant SCI, la chimie radicalaire interférente, notamment la formation de radicaux OH par décomposition unimoléculaire des SCI, a été supprimée par l'ajout d'un excès de cyclohexane comme piègeur de ces radicaux.

Nous avons utilisé un spectromètre de masse à transfert de proton (PTR-MS) en mode NH₄⁺ afin d'assurer le suivi en temps réel des concentrations des réactifs pendant les expériences. En suivant la décroissance relative des analytes dont les constantes de vitesse sont connues, en parallèle de celle des composés cibles, nous avons pu extraire les constantes de vitesse relatives pour les réactions de CH₂OO avec divers acides carboxyliques et alcools. Ces mesures ont été interprétées à l'aide d'un modèle adapté, qui a reproduit avec succès à la fois la cinétique de disparition des réactifs et les profils de formation de certains produits. Ce modèle a également permis d'estimer les concentrations de CH₂OO et d'autres radicaux secondaires (par exemple, OH, HO₂, RO₂ et RO) générés pendant

l'expérience. Cela nous a permis de vérifier que la contribution de la chimie radicalaire secondaire à la cinétique observée était négligeable, garantissant que les profils de décroissance reflètent des réactions bimoléculaires véritables avec CH_2OO .

Nos résultats confirment que la réactivité des SCI varie fortement selon le groupe fonctionnel du co-réactif. Les acides carboxyliques réagissent rapidement avec les SCI, avec des constantes de vitesse atteignant $10^{-10} \text{ cm}^3 \text{ molécule}^{-1} \text{ s}^{-1}$, et une formation de produits cohérente avec une insertion dans la liaison O–H menant à des hydroperoxydes α -alkoxyacyles. En revanche, les alcools se sont révélés bien moins réactifs, nécessitant des concentrations plus élevées en SCI pour une conversion mesurable. Malgré cela, des hydroperoxydes α -alkoxyles et des formates issus de l'insertion dans les alcools ont pu être identifiés, ce qui souligne la sensibilité de la méthode.

En résumé, ces résultats enrichissent la base de données cinétique des réactions de SCI et démontrent que la méthode des vitesses relatives développée au cours de ce travail de thèse permet d'explorer efficacement des espèces peu volatiles ou peu réactives qui ne sont pas adaptées aux méthodes absolues de détermination de constantes de vitesse de réaction. Au-delà de CH_2OO , d'autres réactions d'ozonolyses d'alcènes symétriques pourraient également être utilisées dans cette approche pour générer in situ différents SCI, ouvrant ainsi la voie à l'étude cinétique d'un spectre plus large d'intermédiaires de Criegee. L'analyse des produits a également révélé que les réactions d'insertion des SCI entraînent l'incorporation d'atomes supplémentaires de carbone et d'oxygène dans les molécules mères, formant ainsi des composés plus lourds et moins volatils, plus susceptibles de se répartir dans la phase condensée ou de participer à la nucléation particulaire. Ces produits à faible volatilité peuvent ensuite subir des réactions d'oligomérisation, diminuant encore leur volatilité, un phénomène récemment corroboré par des observations de terrain en Amazonie. Ainsi, la connaissance de la cinétique des SCI et du devenir de leurs produits est essentielle pour comprendre le rôle potentiel de l'ozonolyse dans la formation d'aérosols organiques secondaires (SOA) dans l'atmosphère.

Chapitre 4 : Cinétique en phase gazeuse des hydroperoxydes – une famille de composés chimiques, issue de nombreux mécanismes chimiques atmosphériques, peu étudiée.

Dans le chapitre précédent, les réactions d'insertion des SCI avec divers co-réactifs se sont révélées être une source fiable d'hydroperoxydes fonctionnalisés (ROOHs) formés lors de la dégradation d'alcènes. En réalité, les ROOHs sont issus d'une multitude de mécanismes oxydants. Au-delà de l'ozonolyse, l'une des voies de formation atmosphérique les plus importantes implique les réactions d'auto- et de co-combinaison des radicaux peroxy (RO_2). Par exemple, la combinaison de RO_2 avec HO_2

génère des ROOHs avec un rendement élevé en conditions pauvres en NO_x. En outre, l'autoxydation par isomérisation via transfert d'hydrogène (H-shift) au sein des radicaux RO₂, suivie de l'ajout d'O₂, produit des molécules hautement oxygénées (HOMs), qui contiennent fréquemment plusieurs groupements –OOH. Ces composés sont d'une grande importance atmosphérique, tant en phase gazeuse que particulaire. En phase gazeuse, les hydroperoxydes peuvent subir une oxydation ou une photolyse, libérant des radicaux OH et agissant ainsi comme sources secondaires de radicaux. Ils peuvent aussi se fragmenter thermiquement ou par photolyse, générant des radicaux oxygénés susceptibles d'initier de nouvelles chaînes réactionnelles. En raison de leurs propriétés fonctionnelles – forte polarité et solubilité modérée dans l'eau – ils contribuent efficacement à la croissance des particules et à la formation d'aérosols organiques secondaires (SOA). En phase condensée, ils peuvent également servir de source de peroxyde d'hydrogène, de radicaux peroxy ou alkoxy, et agir comme oxydants, par exemple en oxydant le soufre (IV) en soufre (VI), facilitant ainsi la formation d'aérosols sulfatés.

Malgré leur rôle central dans les processus d'oxydation atmosphérique, la cinétique en phase gazeuse des hydroperoxydes reste encore largement méconnue. Seules quelques constantes de vitesse de réaction avec le radical OH ont été déterminées expérimentalement pour les ROOHs. Cette rareté s'explique principalement par leur forte instabilité thermique, qui pose de graves risques d'explosion lors des processus de synthèse, d'isolation et de stockage. Ces contraintes de sécurité limitent la gamme d'hydroperoxydes pouvant être manipulés en toute sécurité en laboratoire, notamment en raison de la pureté élevée souvent requise pour les études cinétiques. D'autres limitations proviennent de difficultés analytiques : contrairement aux COV traditionnels, les hydroperoxydes ne possèdent pas de chromophores forts, ce qui les rend difficilement détectables par spectroscopie UV-visible. Leur instabilité rend également leur échantillonnage et leur séparation complexes via les techniques classiques de chromatographie en phase gazeuse. Leur faible volatilité les rend sujets à des pertes par adsorption sur les surfaces, compliquant leur introduction fiable dans les systèmes expérimentaux dédiés aux études cinétiques et rendant les déterminations de constantes de vitesse par les méthodes absolues plus difficiles.

Par conséquent, dans ce chapitre, nous avons mis en œuvre une stratégie de génération in situ des ROOHs en phase gazeuse à l'aide d'une chambre de simulation atmosphérique de grand volume. Plus précisément, nous avons utilisé des réactions d'ozonolyse d'alcènes pour générer des SCI, qui en réagissant par la suite avec des acides carboxyliques sélectionnés forment directement des hydroperoxydes α -alkoxyacyliques. Il est à noter que cette approche ne se limite pas aux alcènes symétriques ; au contraire, l'utilisation d'alcènes asymétriques permet la formation de plusieurs SCI,

offrant ainsi la possibilité de générer une diversité d'espèces ROOH. Les hydroperoxydes ainsi produits ont été détectés et suivis en temps réel à l'aide d'un spectromètre de masse à transfert de proton (PTR-MS) fonctionnant en mode NH_4^+ , offrant à la fois sensibilité et sélectivité pour ces composés multifonctionnels peu volatils. En complément, nous avons également mené des mesures sur le *tert*-butyl hydroperoxyde, l'un des rares ROOHs disponibles dans le commerce, en tant que composé modèle pour valider et enrichir nos observations.

Des expériences supplémentaires ont été consacrées à l'élucidation de leurs réactions d'oxydation en phase gazeuse, avec une attention particulière portée à leur réactivité vis-à-vis des principaux oxydants atmosphériques, notamment les radicaux OH, NO_3 et les intermédiaires de Criegee. Pour les expériences impliquant le radical OH, afin d'éliminer toute interférence due à la photolyse des hydroperoxydes et d'isoler la voie d'oxydation par OH, toutes les mesures ont été effectuées dans l'obscurité. L'ozonolyse du tétraméthyléthylène (TME) a ainsi été utilisée comme source efficace de radicaux OH in situ, grâce à la réactivité particulière de l'intermédiaire de Criegee produit, l'oxyde d'acétone, qui subit une décomposition unimoléculaire rapide générant des radicaux OH avec un rendement quasi unitaire, tout en contribuant de manière négligeable à la formation de SCI stabilisés dans ce système. Pour étudier l'importance de l'oxydation nocturne, les radicaux NO_3 ont été générés in situ par l'introduction contrôlée d'ozone et de monoxyde d'azote. Afin d'évaluer d'éventuelles réactions d'oligomérisation impliquant les intermédiaires de Criegee, l'ozonolyse de l'éthène a été utilisée comme source de CH_2OO .

Dans ce contexte, nous avons déterminé la réactivité vis-à-vis de OH de deux hydroperoxydes α -alkoxyacyliques bien définis : l'acétate d'hydroperoxyméthyle et l'acétate de 1-hydroperoxyéthyle. Les constantes de vitesse obtenues ont montré une bonne cohérence et linéarité entre les expériences. Les réactions de ces hydroperoxydes avec les radicaux NO_3 ont également montré une décroissance mesurable, mais les constantes de vitesse dérivées étaient environ trois ordres de grandeur inférieures à celles des radicaux OH. Par ailleurs, la réactivité de l'hydroperoxyde de *tert*-butyle vis-à-vis de l'intermédiaire de Criegee a été évaluée et s'est révélée cohérente avec les déterminations absolues antérieures, ce qui soutient la validité de notre méthode relative en chambre de simulation. En revanche, pour l'acétate d'hydroperoxyméthyle-3-méthylbutanoate généré in situ, aucune réactivité significative avec CH_2OO n'a été observée dans nos conditions expérimentales, ce qui nous a permis de ne déterminer qu'une limite supérieure pour sa constante de vitesse.

Chapitre 5 : conclusion et perspectives

Dans ce dernier chapitre, nous revenons sur les résultats expérimentaux présentés dans ce travail, qui offrent collectivement une meilleure compréhension de la nature complexe et multi-générationnelle de la chimie d'oxydation atmosphérique. Cette thèse de doctorat explore des composés chimiquement distincts mais d'importance atmosphérique, issus à la fois de sources anthropiques et biogéniques. Nos résultats démontrent que l'oxydation atmosphérique ne produit pas seulement des gaz traces à longue durée de vie influençant le forçage radiatif, mais génère également des intermédiaires hautement fonctionnalisés et réactifs susceptibles de favoriser la formation d'aérosols organiques secondaires.

En perspective, l'extension des mesures cinétiques à un éventail plus large de produits d'oxydation multifonctionnels reste indispensable, très peu de données étant disponibles pour les fonctions peroxyde, acide peroxy, nitrate organique et peroxyacyl nitrate. Le développement de méthodes in situ améliorées pour les composés instables et peu volatils sera également crucial pour affiner les modèles atmosphériques. En définitive, ce travail contribue à une approche plus mécanistique et prédictive pour évaluer les impacts de la chimie organique complexe sur le climat et la qualité de l'air.

L'ensemble des travaux présentés ci-dessus a été communiqué durant la période de doctorat dans plusieurs conférences internationales, ateliers et séminaires. À ce jour, une partie de ces travaux a donné lieu à une publication dans une revue scientifique de haut niveau, tandis que trois autres articles sont actuellement en cours de soumission ou de rédaction.

Chapter 1:

Introduction

1 Introduction

The atmosphere is the outer layer of the Earth system, it oxidizes pollutants, filters radiation and regulates the climate system, thus protecting ecosystems and human beings. Despite its seeming intangibility, it is a highly structured and chemically active system. Structurally, the atmosphere is layered: the troposphere is closest to the Earth's surface and is the home of weather systems and the bulk of air pollution; above it lies the stratosphere, which is marked by the ozone layer; and extending towards space, there is the mesosphere, thermosphere, and exosphere, each of which has a different thermal gradient and composition (Finlayson-Pitts and Pitts, 2000; Jacob, 1999; Seinfeld, 2016). Compositionally, >99% of the atmosphere constitutes stable dimers of nitrogen and oxygen, and argon, none of which react together under ambient conditions. Yet it is the trace constituents, present in tiny amounts, that exert a disproportionate influence on the chemistry of the atmosphere and Earth's environment (Finlayson-Pitts and Pitts, 2000).

1.1 Scientific background and motivation

A defining feature of the atmospheric transformation lies in its sustained oxidative capacity. Radical species such as hydroxyl (OH), nitrate (NO₃), chlorine (Cl) radicals and ozone (O₃) initiate complex chains of reactions that control the fate of thousands of trace gases (Thompson, 1992). While these reactions help to “clean” the atmosphere, they simultaneously generate a complex array of secondary products. As early as the 1950s, scientists observed that the interaction of sunlight with NO_x and hydrocarbons led to photochemical smog (Davidson, 1998; Haagen-Smit, 1952). Historically, these processes have had other deadly social consequences. The 1943 Los Angeles photochemical haze, the 1952 Great Smog of London, and the 1964 Yokkaichi asthma crisis all marked milestones in recognizing how chemical transformations of pollutants under atmospheric conditions can severely impact public health (Bell et al., 2004; Davidson, 1998; Imai et al., 1967).

Despite technological advances and regulatory progress, air pollution remains a persistent global challenge in the 21st century (WHO, 2019). In rapidly urbanizing regions like East and South Asia, the pollution of tropospheric O₃ and PM_{2.5} are particularly acute (He et al., 2024). Tropospheric O₃, as a potent oxidant, is not only harmful to human respiratory health but also damages crops and ecosystems (Lefohn et al., 2018). PM_{2.5}, which consists of both primary particles and a large fraction of secondary aerosols derived from gas-phase precursors, has been identified as one of the leading environmental risk factors for premature death worldwide (Sangkham et al., 2024; WHO, 2021). These severe health and environmental impacts reflect not only the high levels of exposure but also the

intricate chemical composition of these particles. Although organic aerosols are a major component of PM_{2.5}, the mechanism underlying their formation remains poorly understood, especially regarding processes that involve multifunctional, low-volatility organic compounds (Nakao et al., 2012; Shrivastava et al., 2017).

Parallel to air quality degradation, climate change introduces a different dimension of atmospheric chemical concern (Ravishankara et al., 2015). Some industrial halogenated emissions, such as hydrofluorocarbons (HFCs) and perfluorocarbons (PFCs), exert disproportionately large radiative forcing due to their long atmospheric lifetimes and strong IR absorption in the atmospheric window (Bravo et al., 2010; Hodnebrog et al., 2020). These compounds are characterized by exceptionally high C–F bond dissociation energies, making them remarkably resistant to oxidation by atmospheric radicals and photolytic processes. Their long atmospheric lifetimes range from decades to tens of thousands of years, allowing them to reach the upper atmosphere, where they act as highly efficient infrared absorbers, thereby contributing to long-term radiative forcing (WMO, 2022). For instance, CF₄ is estimated to have an atmospheric lifetime exceeding 50,000 years and a global warming potential (GWP) of 7490 (WMO, 2022). Perfluorooctanoic acid (PFOA) and related perfluoroalkyl substances (PFAS), often produced as oxidation products or industrial intermediates, have been widely detected in surface waters, wildlife, and throughout the global population (De Silva et al., 2020). Their presence underscores the need for understanding both reactive and unreactive trace species in the atmosphere.

As illustrated in Figure 1-1, air pollution and climate change are both representative environmental issues driven by atmospheric chemistry, where notable overlaps exist. Some pollutants like tropospheric ozone and black carbon not only degrade air quality but also act as short-lived climate forcers (Ramanathan and Carmichael, 2008; Shindell et al., 2012). Climate change, in turn, feeds back into the Earth system through impacts such as sea level rise, altered precipitation, droughts, and extreme weather events (Ravishankara et al., 2015). Traditionally, wildfires have been considered as a source of aerosol emissions that degrade local air quality. However, recent study revealed that the heat released from wildfire can enhance wet deposition and suppress horizontal transport, thereby reducing PM_{2.5} concentrations (Ma et al., 2025). Such couplings between air pollution and climate change acting on local to even global scales remain an active area of research (Ma et al., 2025). The key to whether gas or aerosol emissions perturb climate or air quality lies in their chemical properties (Ravishankara et al., 2015): How long do they reside in the atmosphere before being removed or transformed? Where, and to what extent, do they and their oxidation products absorb or scatter

ultraviolet, visible, or infrared radiation? And how do they alter the lifetime or properties of other atmospheric constituents?

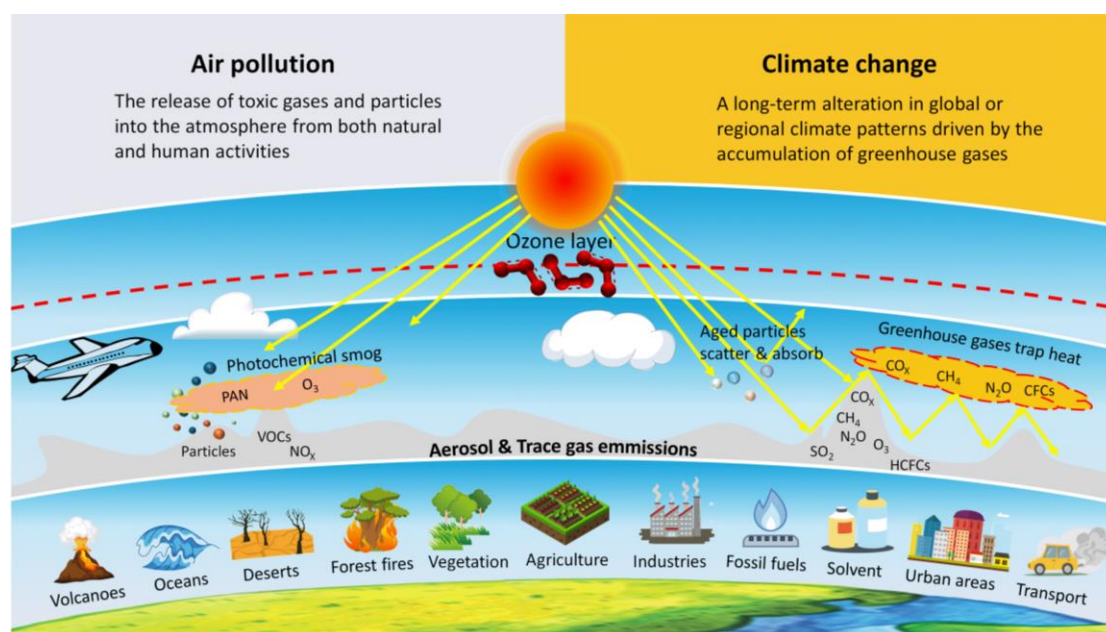


Figure 1-1. Interactions between air pollution and climate change.

To unravel this complex interplay, modern atmospheric chemistry research relies on three complementary approaches (Abbatt et al., 2014): (1) controlled laboratory experiments that simulate atmospheric conditions and isolate specific reactions; (2) *in situ* observations that capture realistic data on different spatial and temporal scales; and (3) numerical modelling that integrates these findings into a predictive framework.

Related to point (1), understanding the reaction kinetics and transformation mechanisms of trace compounds is essential. The atmospheric lifetime, oxidation pathway, and product formation of a molecule hinge on its reactivity with respect to key oxidants. These reactions determine whether a compound will degrade quickly, persist over time, form secondary pollutants, or contribute to climate forcing. While much progress has been made through current kinetic databases, such as (IUPAC, 2025), (Burkholder et al., 2019) and (McGillen et al., 2020), and laboratory measurements, a wide array of emerging and multi-generational atmospheric products, especially those formed through successive oxidation steps, remain poorly characterized (Bianchi et al., 2019).

Since beginning my doctoral studies, I have been drawn to investigating these chemically complex but environmentally significant processes in the atmosphere. This thesis presents kinetic measurements and methodological developments targeting multi-generational atmospheric compounds originating

from both anthropogenic sources (e.g., fluorinated species) and natural emissions (e.g., Criegee intermediates and hydroperoxides).

1.2 Sources and sinks in the atmosphere

The chemical composition of the atmosphere is governed by a dynamic balance between emission sources and sinks. For some of the long-lived fluorinated gases (F-gases) mentioned earlier, this balance is overwhelmingly skewed toward the source side. Their unparalleled molecular stability makes them virtually immune to atmospheric removal, leading to rapid increases in the global average mixing ratio (WMO, 2022). For such species, the priority lies in emission reduction, substitution strategies, and identifying secondary processes that may unintentionally release them.

In contrast, most reactive volatile organic compounds (VOCs), whether biogenic or anthropogenic, eventually undergo conversion toward stable end-products such as CO₂, H₂O, or in the case of F-gases, HF (Atkinson, 2000; Burkholder et al., 2015). In this sense, the atmosphere can be viewed as a giant oxidative reactor, processing a chemically diverse set of volatile compounds into a narrower set of highly stable, often inorganic final end-products. At this point, the key challenge lies in understanding the multigeneration oxidation cascades where VOC emissions yield a rich ensemble of intermediate species with evolving volatility, reactivity and toxicity. These multigenerational species not only influence atmospheric composition, but also link to broader environmental outcomes such as aerosol formation. Advancing our understanding of these transformations requires first characterizing the nature of the precursor emissions and the mechanisms that drive their atmospheric evolution.

The following sections examine in detail the major atmospheric sources and sinks, focusing on the chemical mechanisms that determine how substances are introduced, transformed, and ultimately removed from the atmospheric system.

1.2.1 Emission sources

Currently, tens of thousands of unique gas-phase organic compounds have been measured in the atmosphere, and it is speculated that there may be hundreds of thousands more that have not been observed/measured (Goldstein and Galbally, 2007; Nozière et al., 2015). Most of these compounds are atmospheric oxidation products but a significant number are direct emissions. In field measurements, we often face huge limitations (e.g., due to their low-volatility, thermal instability or instrumental sensitivity) in detecting all reactive species. Nevertheless, total reactivity measurements such as OH loss rate allow us to infer the existence of some “missing” species. Among these, volatile

organic compounds (VOCs) dominate in number and reactivity, yet comprehensive measurements reveal that almost half or more of total reactive organic carbon (ROC) remains uncharacterized (Heald et al., 2020; Hunter et al., 2017; Nölscher et al., 2016).

1.2.1.1 Biogenic emissions

The terrestrial biosphere is a major source of biogenic volatile organic compounds (BVOCs), which represents the largest global input of reactive carbon to the atmosphere, estimated to be around 1000 Tg yr⁻¹, nearly an order of magnitude greater than those from anthropogenic sources (Guenther et al., 2012). A significant fraction of these BVOCs are unsaturated hydrocarbons, which possess one or more carbon-carbon double bonds and thus exhibit high reactivity with atmospheric oxidants such as O₃ and OH radicals (McGlynn et al., 2021).

The single most important BVOCs is probably isoprene (C₅H₈, 2-methyl-1,3-butadiene), as it represents the most abundant non-methane organic and alone accounts for over 50% of the total mass flux of BVOCs (Guenther et al., 2012). However, as important as isoprene undoubtedly is, it is just one among more than 55,000 known terpenoid structures (Chen and Baran, 2009). Geographically, isoprene is primarily emitted by broadleaf deciduous trees (e.g., oak and poplar), with high emissions in tropical and temperate regions, while conifers (e.g., pine and spruce) are the major sources of monoterpenes such as α-pinene and β-pinene (Kesselmeier and Staudt, 1999).

With advancements in analytical techniques, especially proton-transfer reaction–mass spectrometry (PTR-MS) and Orbitrap-based high-resolution instruments, researchers have uncovered an increasingly complex array of BVOCs, including large, low-volatility molecules like sesquiterpenes (C₁₅H₂₄) and diterpenes (C₂₀H₃₂) (Li et al., 2020). These unsaturated olefins, characterized by their high global emissions and reactivities, act as precursors of many highly oxygenated molecules (HOMs) and secondary organic aerosols (SOA), especially under low-NO_x or forest conditions (Caravan et al., 2024; Pullinen et al., 2020). Their atmospheric reactivities, subsequent formation of HOMs, and SOA formation potential will be discussed in detail in Chapter 3 and Chapter 4.

In addition to terpenoids, plants also emit a number of low-molecular weight (C<5) BVOCs, such as alcohols, carbonyls, and organic acids, which often originate from primary metabolism or abiotic stress (Argueso et al., 2007; Fall, 2003; Kreuzwieser et al., 1999). Many BVOCs function as semiochemicals, chemical signals that mediate intra- and interspecies interactions (Laothawornkitkul et al., 2009). Such emission can be used to deter herbivores, attract their predators, or warn neighbouring plants (Dicke, 1986; Ninkovic et al., 2021). They also use floral scents to attract pollinators and emit allelopathic

volatiles to suppress competitors (Laothawornkitkul et al., 2009). Beyond plants, a wide variety of insects and other animals release pheromones that can be used to attract mates, among other uses (Fleischer and Krieger, 2018). Microorganisms also contribute BVOCs, particularly in soils and wetlands, affecting nutrient cycling, plant growth, and microbial interactions (Tang et al., 2019).

1.2.1.2 Anthropogenic emissions

One defining feature of anthropogenic volatile organic compounds (AVOCs) is their chemical diversity. Recent cross-country analyses suggested > 350,000 chemicals and chemical mixtures are registered for production and use worldwide (Wang et al., 2020). This originates from transportation, fossil fuel combustion, industry, solvent use, and residential practices as shown in Figure 1-1. In densely populated and industrialized regions, AVOC can rival or even exceed biogenic emissions on a local scale (McDonald et al., 2018; Tamrakar et al., 2025; Warneke et al., 2007).

One of the most significant consequences of anthropogenic emissions is their climate-forcing effect, primarily driven by long-lived greenhouse gases (GHGs), such as carbon dioxide (CO₂), methane (CH₄), nitrous oxide (N₂O) and F-gases mentioned above. CO₂ and CH₄ are perhaps the most pervasive greenhouse gases, accounting for over 75% of total anthropogenic GHG emissions by mass (Friedlingstein et al., 2022).

By contrast, the volumes of F-gases that are released to the atmosphere are low. However, because of their disproportionately high radiative effects, and because of their potentially long lifetimes, their overall radiative forcing effect is high enough that they warrant special attention (Burkholder et al., 2015). Since their introduction in the 1930s, these compounds have been widely employed in refrigeration, aerosol propellants, foam blowing agents, flame retardants, and various other industrial applications, initially replacing toxic, flammable and explosive natural alternatives (Solomon, 1999). Figure 1-2 summarizes the evolution of synthetic F-gases and the relevant regulatory frameworks that have shaped their development. First generation F-gases, chlorofluorocarbons (CFCs), were extensively used throughout the 20th century until they were found to release reactive chlorine atoms in the stratosphere, leading to catastrophic ozone depletion. This discovery prompted the 1987 Montreal Protocol, under which CFCs were gradually phased out and replaced first by hydrochlorofluorocarbons (HCFCs), and later by hydrofluorocarbons (HFCs). The former, as a transitional substitute, still depletes the ozone layer, albeit to a lesser extent. The latter has a low ozone depletion potential, but its longer atmospheric lifetime also results in a higher global warming potential. To address this, the Kigali Amendment to the Montreal Protocol, adopted in 2016, mandated the accelerated phase-out of HFCs in favour of low-GWP alternatives. Hydrofluoroolefins

(HFOs) and hydrochlorofluoroolefins (HCFOs) are the current leading next-generation alternatives, characterized by the presence of carbon-carbon double bonds. Their olefinic structures facilitate rapid reaction with atmospheric radicals such as OH, resulting in short atmospheric lifetimes ranging from a few days to weeks (McGillen et al., 2023). Consequently, these compounds exhibit zero ODP and very low direct GWPs (WMO, 2022).

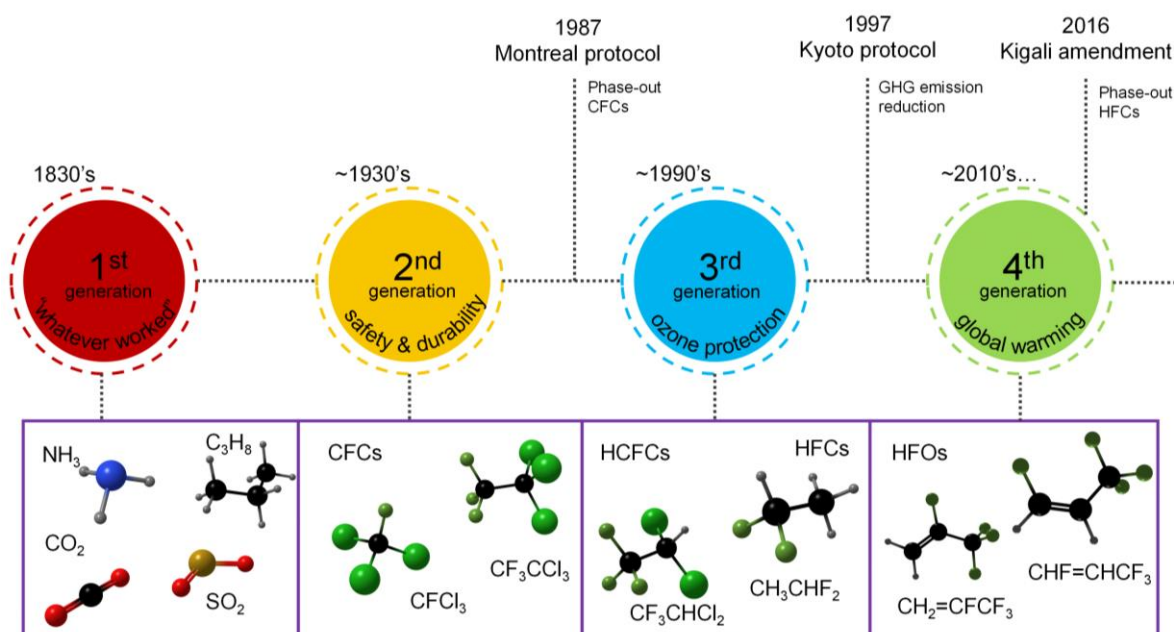


Figure 1-2. Evolution of synthetic Fluorinated gases with the international regulations targeting ozone depletion and global warming. Adapted from (Pérez-Peña et al., 2023).

However, their rapid atmospheric degradation does not preclude environmental concerns. The oxidation chain reactions initiated by OH or O_3 lead to the fluorinated carbonyls and acids, notably trifluoroacetic acid ($\text{CF}_3\text{C}(\text{O})\text{OH}$) (Henne et al., 2012) and trifluoroacetaldehyde (CF_3CHO) (Baasandorj et al., 2011; Javadi et al., 2008; Sulbaek Andersen et al., 2018). $\text{CF}_3\text{C}(\text{O})\text{OH}$ is highly soluble so that it can be rapidly removed from the atmosphere by wet deposition. However, its chemical stability leads to strong persistence and accumulation potential in aquatic environments, where it has been detected in rivers, oceans, crops, and even food products (Scheurer et al., 2017). In parallel, ongoing debate centres on whether or not the photodecomposition of CF_3CHO could produce CHF_3 (HFC-23, fluoroform), where the photolysis is considered to be another main fate of CF_3CHO besides OH oxidation (Chiappero et al., 2006; Dodd and Smith, 1957; Pearce and Whytock, 1971; Sellevåg et al., 2004; Sulbaek Andersen et al., 2023; Sulbaek Andersen and Nielsen, 2022; Thomson et al., 2025; Van Hoomissen et al., 2025). CHF_3 is a compound known as one of the most potent greenhouse gases with a 100-year global warming potential of ~ 14700 (WMO, 2022), which means that the formation of just one ton of CF_3H is equivalent to emitting 14,700 tons of CO_2 . This has raised growing concerns over

the indirect greenhouse gas emissions resulting from the atmospheric degradation of HFOs, despite their low direct GWP. This issue will be explored further through dedicated experimental investigations in Chapter 2.

1.2.1.3 Geological emissions

The solid Earth is a natural source of many inorganic gases such as CO₂, SO₂, H₂S and CH₄, which are emitted into the atmosphere primarily via volcanic eruptions, geothermal activity, and diffuse crustal degassing (Kerrick, 2001; Oppenheimer et al., 2011). While these fluxes are often steady on geologic timescales, episodic events like volcanic eruptions can lead to sharp, short-term atmospheric inputs. In parallel, organic matter buried in sedimentary basins undergoes thermal maturation under high temperature and pressure over millions of years, a process known as “catagenesis”, leading to the formation of crude oil and natural gas (Tissot and Welte, 1984). These hydrocarbon-rich reservoirs are often sealed by impermeable cap rocks, however, in places where natural seepage occurs (such as tar pits or faults), light VOCs (e.g., alkanes, benzene and toluene) can escape into the atmosphere (Kvenvolden and Rogers, 2005).

1.2.1.4 Oceanic emissions

The ocean spans over 70% of Earth’s surface and functions as a vast air-water interface (Falkowski et al., 1998). Depending on the concentration gradient across this boundary and the partitioning behaviour, it can act either as a source or a sink for numerous trace gases (Carpenter and Nightingale, 2015). Marine emissions of inorganic gases are generally characterized by sulfur, nitrogen and halogen compositions (Carpenter et al., 2012).

Recent advances have turned attention to the ocean’s role in supplying VOCs, marked by some BVOCs (e.g., isoprene and monoterpenes), alcohols (e.g., methanol and ethanol), and a suite of sulfur-containing (e.g., dimethyl sulfide) and halogenated VOCs (e.g., bromoform, methyl iodide) are released via phytoplankton metabolism, bacterial degradation, and abiotic photochemical reactions (Carpenter et al., 2012). In addition, sea spray aerosol (SSA), generated by bubble-bursting at the ocean surface, contains a large number of organic species, many of which possess surfactant properties and some of which will then be volatilized or repartitioned into the gas phase (Rasmussen et al., 2017).

1.2.2 Sinks

Atmospheric chemistry is fundamentally oxidative in nature, and the oxidative aging of organic compounds tends to follow a clear direction. Molecules that enter the atmosphere undergo a sequence of chemical transformations, gradually reaching higher carbon oxidation states (OS_C) as illustrated in Figure 1-3. The oxidation mechanisms for light VOCs are relatively straightforward, with the canonical example being conversion of methane ($OS_C = -4$) into formaldehyde ($OS_C = 0$), CO ($OS_C = +2$) and ultimately CO_2 ($OS_C = +4$). However, most VOCs will undergo additional intermediate steps such as functionalization, fragmentation, and oligomerization (Kroll et al., 2011).

Photochemistry further shapes the fates of molecules by introducing wavelength-dependent processes. Absorption of solar radiation by specific functional groups can trigger bond cleavage, isomerization, or even direct mineralization, bypassing the radical-driven reaction chains. Oxidation and photolysis processes will be detailed below. In addition, heterogeneous and multiphase processes, that increase complexity exponentially in a non-negligible way, will be briefly discussed.

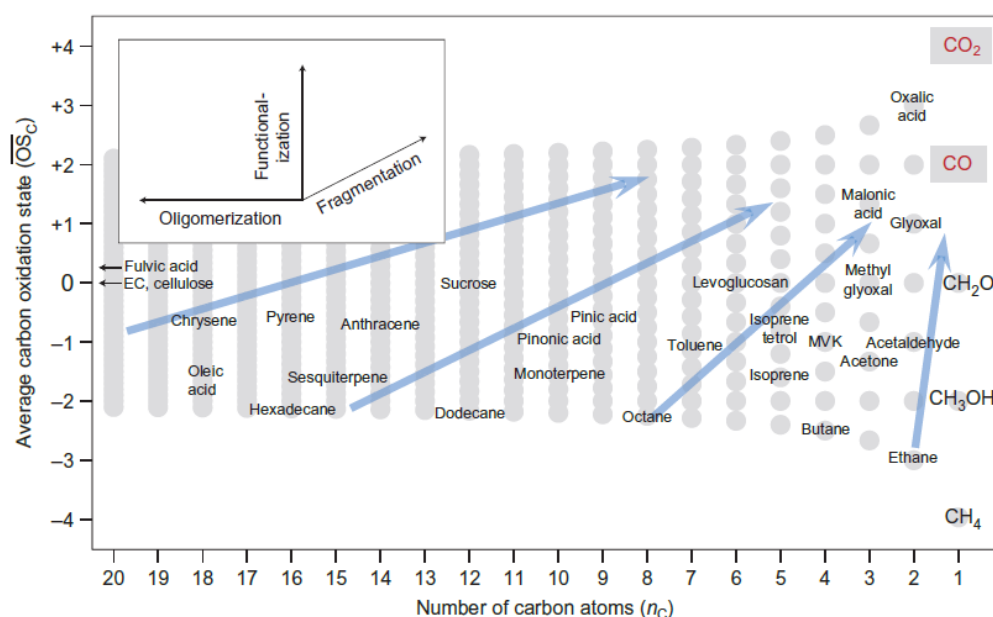


Figure 1-3. Possible combinations of average carbon oxidation state (OS_C) and number of carbon atoms (n_C) for stable organic molecules. Taken from (Kroll et al., 2011).

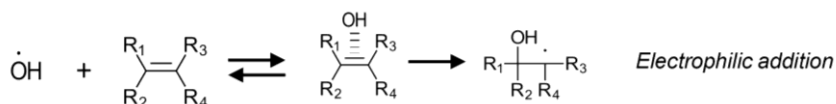
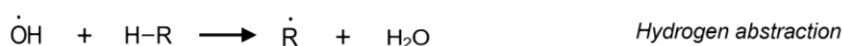
1.2.2.1 Oxidation

Atmospheric oxidation is initiated by primary reactions with atmospheric oxidants, involving hydroxyl radicals (OH), nitrate radicals (NO_3), ozone (O_3), chlorine atoms (Cl), and ozonolysis-derived Criegee intermediates (CIs). The relative importance of each of these oxidants depends strongly on the

chemical structure of the organic molecules, as well as environmental factors including time of the day (daytime vs. nighttime), geographic location (inland vs. coastal), and the presence of co-emitted species that modulate oxidant concentrations.

Oxidation rates determine the atmospheric lifetime and accumulation potential of organic molecules. In this respect, OH radical is generally considered to be the most important oxidant, since the combined effect of its relatively high rate coefficients with most atmospheric organics and its substantial mixing ratios in the daytime results in large loss rates (therefore a short lifetime). By contrast, O₃ reactions, despite having relatively low rate coefficients (e.g., toward alkenes), can be important because the high mixing ratios of O₃ can still lead to substantial loss rates.

Two primary reaction mechanisms dominate VOC oxidation: hydrogen abstraction and electrophilic addition. For instance, OH, NO₃ and Cl radicals can abstract hydrogen atoms from saturated or functionalized carbon sites, while OH, O₃, NO₃ and Cl can add electrophilically to carbon–carbon double bonds. Taking OH radical as an example, its simplified bimolecular oxidation mechanisms are as follows:



The dominant pathway for a given molecule depends strongly on its degree of unsaturation, substitution pattern, and functional group composition (Mellouki et al., 2003). Figure 1-4 summarizes and compares the experimentally determined OH reactivities of various compound classes based on their primary functionality.

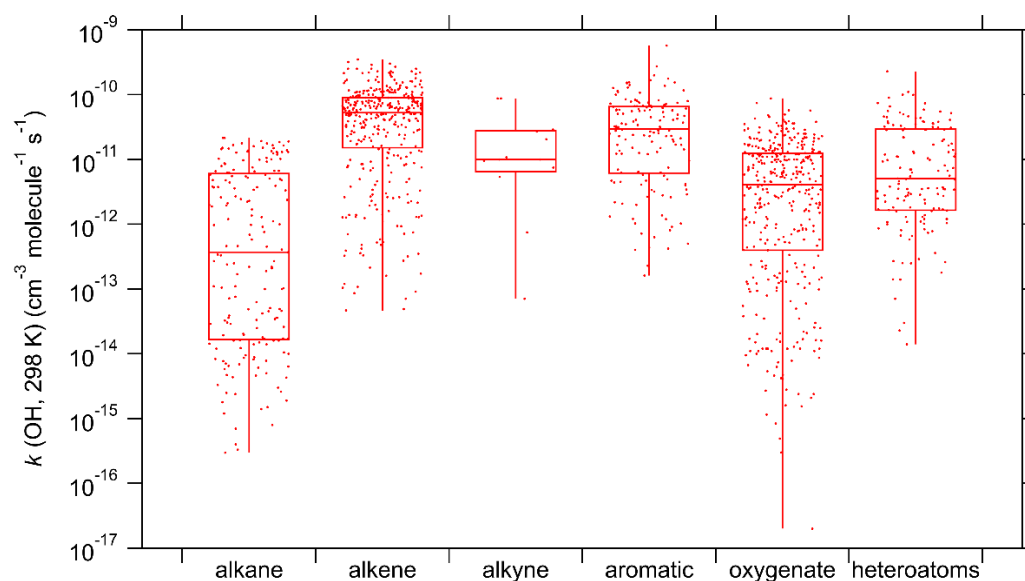


Figure 1-4. Box plot comparing the gas-phase reactivities of various functional groups with hydroxyl radicals (OH). The “heteroatoms” category includes compounds containing N, S, P or Si elements. Since some compounds may contain multiple functional groups, each was assigned to the category corresponding to its most reactive site (e.g., oxygenated alkenes are classified under “alkene” due to the dominant C=C reactivity). Data used in this plot are based on the compilation presented by (McGillen et al., 2020).

Take the simplest case of alkanes, they contain only C-H and C-C bonds structurally, resulting in a relatively uniform electron distribution. In this case reactions with OH radicals proceed exclusively via hydrogen abstraction. Reactivity increases slightly with extended carbon chains or branching, due to the reduced bond dissociation energies (BDEs) at secondary and tertiary C-H site (Atkinson, 2003). In contrast, haloalkanes—particularly fluorinated species—exhibit markedly reduced OH reactivity due to strong electron-withdrawing effects of C–F and other halogenated bonds, which generally increase the BDEs of adjacent C–H bonds, although not in a straightforward manner (McGillen et al., 2024). As shown in Figure 1-5, the OH rate coefficients of haloalkanes (containing one or more halogens) are substantially smaller than those of non-halogenated analogs.

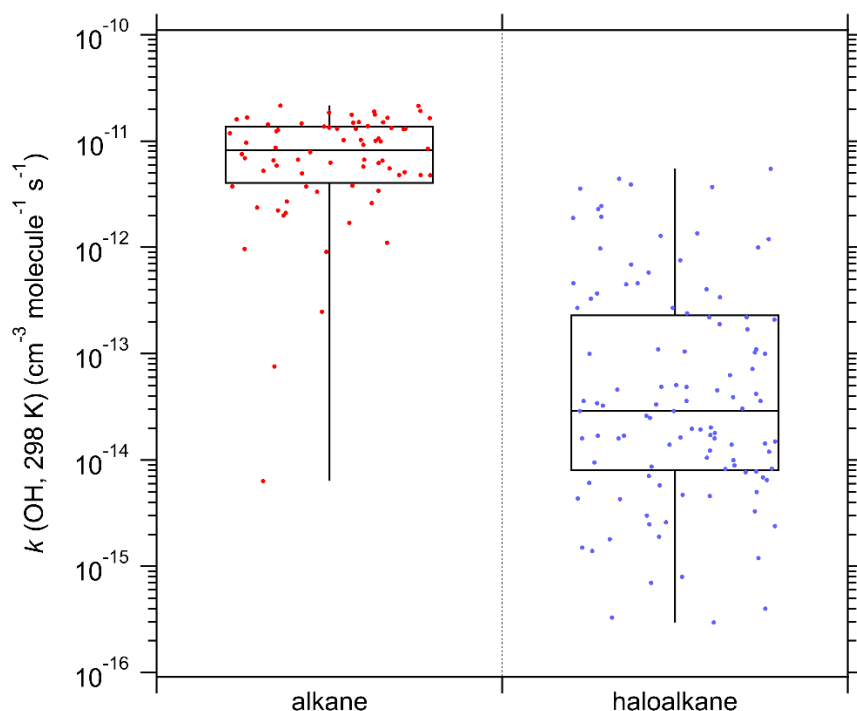


Figure 1-5. A box plot comparing the gas-phase rate coefficients ($k(\text{OH}, 298 \text{ K})$) of non-halogenated alkanes and halogenated alkanes with OH radicals. Data used in this plot are based on the compilation presented by (McGillen et al., 2020).

Compared to their saturated analogues, unsaturated compounds exhibit markedly enhanced reactivity due to electrophilic addition mechanism, whereby OH interacts with the π system (such as those present in olefinic, furanic, and benzenoid structures) to form a pre-reactive complex, subsequently yielding a β -hydroxyalkyl radical (Atkinson, 2003). The high rate coefficients of this addition pathway render hydrogen abstraction reactions negligible for many of these species. A striking example is HFOs mentioned in section 1.2.1.2, which contain both C=C bonds and electronegative substituents as shown in Figure 1-6, react with OH almost exclusively via electrophilic addition (Michelat et al., 2022).

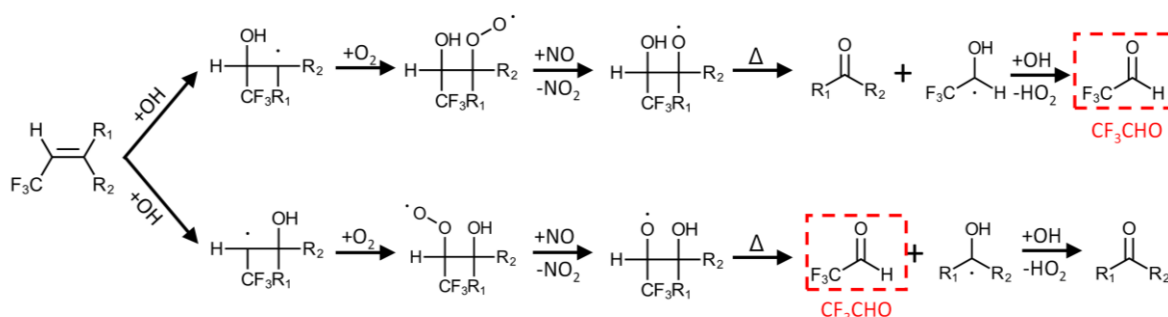


Figure 1-6. Schematic mechanism of OH electrophilic addition to hydrofluoroolefins (HFOs) containing “-CF₃CH=” moiety. As discussed in Section 1.2.1.2, the formation of CF₃CHO has been observed as a major degradation product in multigenerational oxidation of HFOs in the atmosphere.

In alkynes, OH adds across the π system to form vinyl-type radicals. However, their linear geometry and more localized π -electron density generally result in lower reactivity than alkenes (Atkinson and Aschmann, 1984). In benzenoid compounds, OH adds to the aromatic ring, forming a transient σ -complex that temporarily disrupts aromaticity. This disruption of conjugation imposes an energetic penalty, making the addition step typically rate-limiting and may compete with hydrogen abstraction at alkyl side chains when present (Finlayson-Pitts and Pitts, 2000). The “oxygenates” category includes structurally diverse species such as alcohols, aldehydes, ketones, acids, and organic peroxides, many of which are formed as secondary oxidation products. Their reactivity toward OH varies widely depending on functional group combinations, with polar or electron-withdrawing groups often enhancing the rate via inductive or hydrogen-bonding interactions (Kwok and Atkinson, 1995). Compounds containing heteroatoms such as nitrogen (N), sulfur (S), or phosphorus (P) also exhibit highly variable OH reactivity, though they are not the primary focus of this work.

Similar to OH, NO_3 and Cl engage in both hydrogen abstraction and electrophilic addition mechanisms. NO_3 is generally considered to be the primary atmospheric oxidant in the nighttime and particularly show a high reactivity towards unsaturated species such as alkenes and furans (Atkinson, 2000). Hydrogen abstraction with NO_3 is relatively slow compared to OH, but a much higher reactivity is observed for aldehydic C-H bonds (Wayne et al., 1991). Cl atoms are traditionally considered to be important only in coastal environment. However, recent evidence has highlighted the potential significance of nitryl chloride (ClNO_2) as a reservoir of Cl even in inland environment (Thornton et al., 2010). Cl is a highly reactive radical that reacts efficiently through both hydrogen abstraction and electrophilic addition mechanisms. In many cases, hydrogen abstraction by Cl can even compete with addition. The high reactivity in both pathways arises from the strong electronegativity and low activation barriers associated with Cl, allowing it to compete effectively with OH and NO_3 in specific environments (Simpson et al., 2015).

O_3 as an oxidant is less reactive but more selective than OH. It reacts negligibly with saturated compounds and instead mainly react through 1,3-cycloaddition to alkenes, leading to the formation of an energized primary ozonide (POZ). Once formed, this transient intermediate rapidly decomposes to yield an excited Criegee intermediate (CI) and a carbonyl co-product, as illustrated in Figure 1-7.

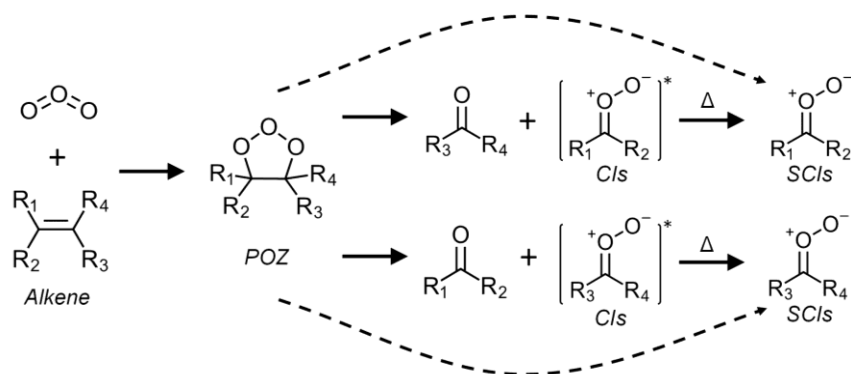


Figure 1-7. Schematic mechanism of ethene ozonolysis to produce Criegee intermediates.

The nascent CIs are generated with a range of internal energies, a varying proportion of which possess sufficient excitation for prompt decomposition. However, a fraction of these excited CIs can also be collisionally stabilized to form stabilized Criegee intermediate as a reactive oxidant. SCIs could participate in a variety of bimolecular reactions through insertion, cycloaddition and direct addition mechanism depending on co-reactants, as summarized in Figure 1-8. Notably, these bimolecular reactions result in adducts that possess an increased mass and a concomitant reduced volatility, which may help explain the special capacity of ozonolysis reactions to produce secondary organic aerosol. This ozonolysis-initiated pathway is therefore a central focus in this thesis (see chapter 3 and chapter 4).

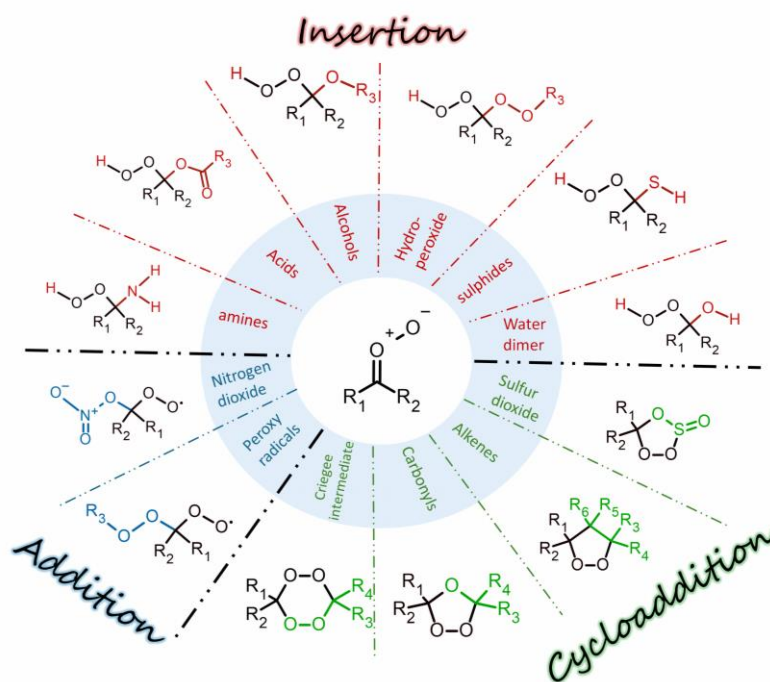


Figure 1-8. Schematic overview of representative bimolecular reaction pathways of stabilized Criegee intermediates (SCIs). Reactions are categorized into insertion (red), direct addition (blue), and cycloaddition (green) mechanisms, depending on the co-reactant class.

1.2.2.2 Photolysis and phototautomerization

Complementary to radical-initiated oxidation, photolysis serves as a direct atmospheric removal pathway in which absorbed solar radiation initiates molecular fragmentation. In the atmosphere, solar radiation reaching the troposphere spans roughly 290 to 700 nm, with UV-B (290–320 nm) and UV-A (320–400 nm) being most relevant for photochemistry. UV-C (<290 nm) is largely filtered by stratospheric ozone and does not reach the lower atmosphere.

Photolysis is fundamentally triggered by photon absorption, whereby quantized energy promotes to an electronic transition, leading to an excited state. This process requires the presence of a chromophore. Upon absorption, electrons are typically promoted from nonbonding (n) or π -bonding orbitals into higher-energy π^* antibonding orbitals, resulting in $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ electronic transitions. The most photochemically active chromophores include carbonyls (e.g., aldehydes and ketones), as well as nitro compounds and organic peroxides.

Carbonyl photolysis often proceeds via multiple competing pathways, including radical and molecular channels. As illustrated in Figure 1-9, two classic photolysis mechanisms of carbonyls are known as Norrish Type I and Norrish Type II reactions. In Norrish Type I, cleavage of the α C–C bond yields an acyloxy radical and an alkyl radical. In Norrish Type II, γ -hydrogen abstraction is followed by intramolecular rearrangement and β -scission, typically producing an alkene and a vinyl alcohol compound.

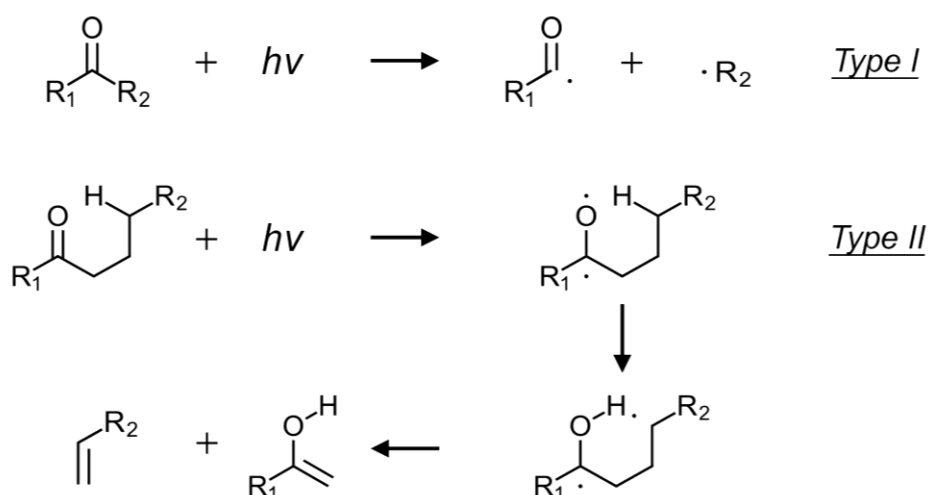


Figure 1-9. Schematic mechanisms of Norrish Type I and Norrish Type II reactions.

The probability that a molecule absorbs a photon at a specific wavelength is described by the absorption cross-section (σ , in units of $\text{cm}^2 \text{ molecule}^{-1}$). It is determined by the molecule's electronic structure and the nature of accessible transitions. Factors such as conjugation, substituent effects,

and molecular symmetry can significantly shift or modulate the absorption spectrum. However, photon absorption does not guarantee bond cleavage. The efficiency that excitation leads to dissociation is determined by quantum yield, which reflects the competition between all relaxation pathways available from the excited state.

Both absorption cross-section and quantum yield are strongly wavelength dependent, their combination with photon flux determines the overall photochemical reactivity for a specific molecule. At shorter wavelengths, higher-lying excited states may become accessible, or bond cleavage thresholds may be reached, enabling new reaction channels or shifting the dominance among existing ones. This variation manifests in wavelength-dependent product distributions and channel-specific quantum yields, even for a single molecule.

Beyond fragmentation, photon-induced electronic excitation can also trigger structural rearrangements such as keto-enol phototautomerization, which could yield several stereoisomers with distinct configurations (Shaw et al., 2018).

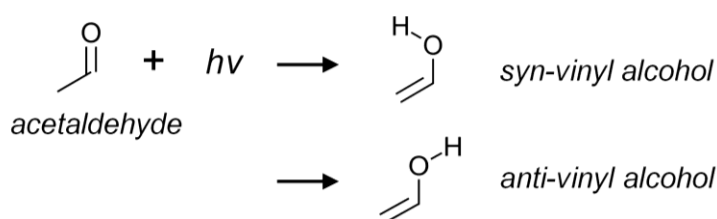


Figure 1-10. Phototautomerization of acetaldehyde resulting in two stereoisomeric vinyl alcohols (syn-/anti-configurations).

1.2.2.3 Others

Several other atmospheric removal processes contribute to the fate of organic compounds, and could be of dominant significance for certain organic molecules under specific environmental conditions. Thermal decomposition, like photolysis, can induce fragmentation in various species. A number of thermally labile compounds, such as peroxyacyl nitrates (PANs), peroxy nitrates, and ClNO_2 , act as NO_x or Cl reservoirs that are readily to be released under elevated temperatures, particularly in the boundary layer (Fischer et al., 2014; Osthoff et al., 2008).

Multiphase interactions represent another key aspect of gas-phase organics being lost and transformed. Wet and dry deposition remove compounds through initial physical-transfer to terrestrial or aquatic surfaces. Water-soluble molecules with high Henry's law constants, as those typically being polar and oxygenated, readily dissolve into cloud droplets and are removed via precipitation, although they may remain in dynamic partitioning between the gas and aqueous phases

(Sander, 2015). Upon dissolution, certain compounds (e.g., those containing acyl halides, anhydrides, or organophosphate groups with electrophilic centers) may engage in a hydrolysis reaction, leading to a permanent chemical transformation (Finlayson-Pitts and Pitts, 2000). Compounds with lower volatility or higher surface affinity may undergo dry deposition through contact with terrestrial surfaces (e.g., vegetation, soil, or surface waters) or adsorption onto leaf cuticles and urban surfaces (Seinfeld, 2016). Uptake into SOA serves as an effective sink for many compounds with high affinity for the organic phase. This uptake is sometimes reversible, but can become effectively irreversible upon subsequent oxidation, oligomerization, or phase transitions within the particle matrix.

Certain exceptional or episodic processes, while rare, can also dominate the atmospheric lifetime of exceptionally persistent species. For example, perfluorinated compounds such as C_2F_6 (hexafluoroethane) exhibit atmospheric lifetime exceeding 500 years, and their removal is governed not by usual radical oxidation, but primarily by high-energy processes such as lightning-induced plasmas (Ravishankara et al., 1994). For such molecules, these physical extremes represent the only effective atmospheric sinks.

However, these processes are not the primary focus of the present thesis and are therefore summarized only briefly here for completeness.

1.4 Challenges in multigenerational air pollution

In the preceding sections, we described two fundamental characteristics of atmospheric chemistry:

- The immense molecular diversity of compounds emitted from various sources;
- Starting from a diverse set of initial reactions, atmospheric transformation unfolds and proceeds through successive oxidation steps.

Once emitted into the atmosphere, VOCs don't follow a single and straightforward degradation pathway. Instead, they undergo an initial set of reactions that branch and propagate into secondary and tertiary channels (Hallquist et al., 2009). The specific route a molecule takes and the distribution of the products depends on its structure and selectivity of atmospheric oxidants toward different reactive sites inside of the molecule. This competitive partitioning across multiple degradation pathways leads to an exponential expansion of product complexity. Each reactive step opens multiple downstream channels that vastly amplify the molecular diversity present in the atmosphere. For example, even for a single precursor compound of moderate structural complexity, such as α -pinene, the number of unique molecular products formed through just a few generations of oxidation can be

staggering. Estimates suggest that α -pinene alone can yield over 500,000 distinct structures via atmospheric processing (Valorso et al., 2011). This phenomenon is referred to as a “combinatorial explosion” (Vereecken et al., 2018).

Part of this complexity arises from the sheer number of potential oxidation sinks, and also the multifunctional nature of reaction intermediates. Figure 1-11 offers concrete evidence for the extensive chemical transformation of VOCs. Panel (a) displays the frequency distribution of functional groups formed per molecule during the simulated atmospheric oxidation of two representative precursors (α -pinene and *n*-octane) using the GECKO-A mechanism (Aumont et al., 2005). These are compared with compounds in the kinetic databases and primary emissions inventories (Carter, 2015; McGillen et al., 2020). The results reveal that α -pinene oxidation leads to substantial formation of highly oxygenated products, such as hydroperoxides (ROOH), organic nitrates, and peroxyacyl nitrates (PANs), which are rarely found in direct emissions. Even a relatively simple molecule like *n*-octane, once subjected to atmospheric oxidation, yields a range of similarly functionalized products. These multifunctional species typically exhibit high polarity and markedly low saturation vapor pressures, predisposing them to partition into the particle phase and thus playing critical roles in secondary organic aerosol (SOA) formation (Ziemann and Atkinson, 2012).

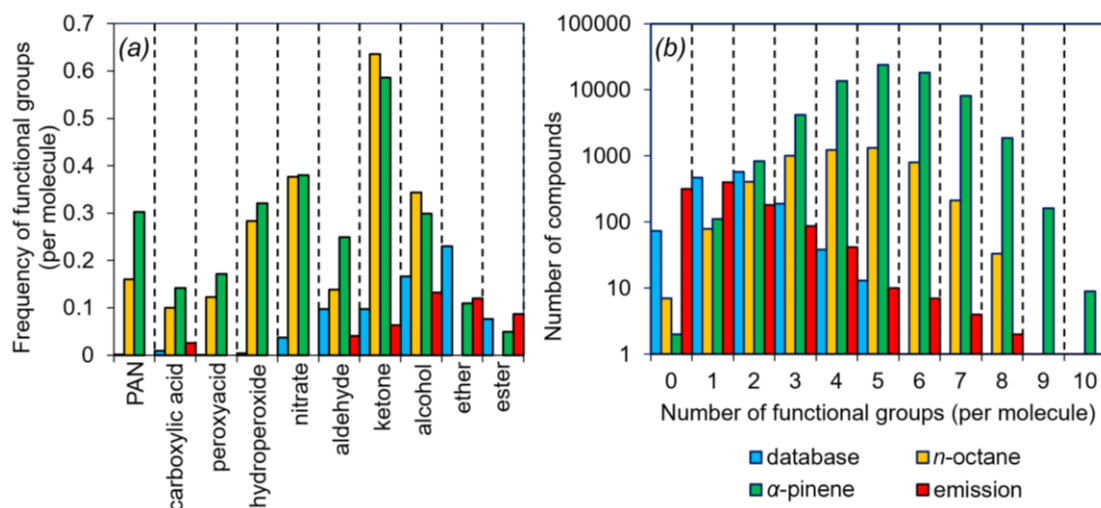


Figure 1-11. Frequency plots comparing the functionalization of compounds within the GECKO-A mechanism of *n*-octane and α -pinene oxidation; a database of anthropogenic emissions (Carter, 2015); and the compounds present in the kinetic database of (McGillen et al., 2020). (Left) Functional groups such as ethers and esters are overrepresented within this database compared with GECKO-A, whereas other functional groups (e.g., nitrates, peroxy acyl nitrates and hydroperoxides) are very poorly represented. (Right) a mismatch is demonstrated between the number of functional groups per molecule in GECKO-A and that of the compounds found in the database. Better agreement is observed in both cases compared with primary emissions profiles. This plot is taken from (McGillen et al., 2020).

However, these functionalized compounds are severely underrepresented in experimental kinetic databases, resulting from several practical and intrinsic challenges. Many of these compounds, such as hydroperoxide, are highly reactive and thermally unstable, making them difficult to isolate, quantify or store (Churchill, 2006; Wang and Shu, 2010). For instance, gas-phase hydroperoxides are prone to photolysis, rapid hydrolysis, and explosive decomposition during handling or analytical preconcentration, severely limiting their routine detection in chamber studies or field campaigns (Commereuc et al., 1997; Hsieh et al., 2014; Zhao et al., 2018). In fact, amongst oxidized species, current kinetic datasets overwhelmingly favor relatively stable species such as ethers, aldehydes, ketones, and alcohols (McGillen et al., 2020), which can be interpreted as due to their ease of handling and reliable quantification via mass spectrometric or spectroscopic techniques. By contrast, hydroperoxides and PAN-type compounds often require specialized derivatization (e.g., PFBHA or CF_3COOH) or sensitive soft-ionization mass spectrometry methods, which are still limited in throughput and application scope (Docherty et al., 2004; Hu et al., 2023).

Furthermore, as panel (b) of Figure 1-11 shows, many of the secondary and tertiary products formed through VOC oxidation are not just singly functionalized, but instead possess multiple functional groups per molecule. While such multifunctional compounds are essential to the oxidative evolution and fate of organics in the atmosphere, their characterization remains sparse. Few compounds with more than three functional groups have been structurally resolved, and the vast combinatorial diversity (as implied by GECKO-A simulations) far outpaces current analytical capabilities. This leaves a major knowledge gap in understanding their kinetics, atmospheric lifetimes, and impacts on processes such as SOA formation, cloud condensation nuclei activation, and heterogeneous chemistry.

1.5 Research framework and outline of the thesis

To better understand the atmospheric evolution of organic compounds and their role in secondary pollution formation, this thesis focuses on selected chemical systems that exemplify multigenerational processing and the emergence of underrepresented intermediates. These compounds are linked to both anthropogenic and biogenic sources, which are explored for two contrasting systems:

Firstly, the atmospheric degradation of synthetic fluorinated gases currently released from industrial emissions may produce greenhouse gases far exceeding their parent compounds, leading to a significant increase in their indirect global warming potential (McGillen et al., 2023).

Secondly, considering the abundance of unsaturated alkenes emitted from biogenic sources, their ozonolysis reactions lead to the formation of substantial quantities and a wide variety of Criegee

intermediates (Wang et al., 2025). The subsequent bimolecular reactions of these reactive intermediates generate multifunctional products, such as hydroperoxides, which may represent important yet underexplored contributors to downstream chemical evolution and secondary organic aerosol formation.

Chapter 1 lays the conceptual groundwork by characterizing atmospheric organic compounds in terms of their diverse sources and removal pathways. It emphasizes how atmospheric transformation unfolds through multigenerational oxidation, branching reaction channels, and multifunctionalization, all of which contribute to the immense complexity of atmospheric chemistry.

Chapter 2 investigates the photochemical degradation of trifluoroacetaldehyde (CF_3CHO), a key oxidation product of hydrofluoroolefins (HFOs) and other fluorinated precursors. By examining its wavelength-dependent photolysis under tropospheric conditions, this chapter highlights its potential role as a source of HFC-23 (Fluoroform, CHF_3), one of the most potent greenhouse gases currently known.

Chapter 3 develops a new relative rate kinetic technique for stabilized Criegee intermediates (SCIs). These reactive carbonyl oxides are central intermediates in alkene ozonolysis. Due to their transient nature and the challenges associated with absolute rate measurements, existing bimolecular kinetic data on SCIs remain very sparse. This chapter introduces a chamber-based strategy using ethene as a symmetric precursor to generate a single SCI species (CH_2OO), which reacts competitively with both reference and target compounds. The method is validated for reactions with acids and alcohols, revealing structure–reactivity trends and enabling comparisons with previously reported rate coefficients.

Chapter 4 investigates the gas-phase oxidation of hydroperoxide esters (ROOH) synthesized *in situ* via a large-volume chamber ozonolysis system. These compounds represent late-generation, highly multifunctional products that incorporate multiple reactive motifs and possess substantial potential for secondary organic aerosol formation. Due to their instability and high reactivity, ROOH presents explosive hazards during synthesis, isolation, and storage, rendering their atmospheric behavior largely unknown. This chapter examines their bimolecular reactions with key atmospheric oxidants including OH , NO_3 radicals and Criegee intermediates.

Chapter 5 summarizes the major findings of this thesis and gives an outlook into further possible research work.

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Chapter 2:

The potential contribution of Trifluoroacetaldehyde (CF_3CHO) photolysis to unaccounted-for atmospheric sources of controlled substance HFC-23 (CHF_3)

2.1 Introduction

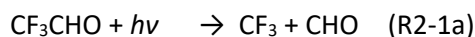
Synthetic fluorinated gases (F-gases) have long been a major product of industrial chemistry and remain a continuing focus of the atmospheric chemistry community. As outlined in Chapter 1, Section 1.2.1.2, the historical evolution of anthropogenic F-gases has been well-established: from the widespread use of chlorofluorocarbons (CFCs) in the mid-20th century, to the subsequent restrictions on hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs), and most recently to the emergence of unsaturated hydrofluoroolefins (HFOs) and hydrochlorofluoroolefins (HCFOs) as replacements. These fourth-generation compounds are often promoted as environmentally benign because of their short atmospheric lifetimes and correspondingly low direct radiative forcing (Wallington et al., 2015). However, the presence of the C=C double bond makes them highly susceptible to rapid atmospheric degradation, during which fluorinated carbonyls can be generated as important transient reservoirs of fluorine (Burkholder et al., 2015).

Among them, trifluoroacetaldehyde (CF_3CHO) is considered to be particularly important and is expected to be formed during the atmospheric degradation of a wide variety of fluorinated precursors, including HFCs, HCFCs, halons, hydrofluoroethers and short-lived HFOs and HCFOs that contain CF_3CH_2- or $\text{CF}_3\text{CH}=\text{}$ moieties (see Table 2-1) (Burkholder et al., 2015). CF_3CHO is often produced in near-unit yield through OH-initiated oxidation chains of these precursors, and has therefore been closely associated with the secondary environmental impacts of F-gases (Javadi et al., 2008; Thomson et al., 2025). The strongly electron-withdrawing CF_3 substituent red-shifts the $n \rightarrow \pi^*$ transition of the carbonyl chromophore into longer wavelengths of actinic range (≥ 290 nm), exhibiting appreciable absorption up to ~ 340 nm ($\sigma \approx 10^{-20}$ cm² molecule⁻¹) (Keller-Rudek et al., 2013), in contrast to most carbonyls whose absorption drops off steeply beyond 300 nm. This red-shifting enables CF_3CHO to undergo efficient photolysis under tropospheric conditions. Likewise, the fluorination of methyl group reduces electron density in the π orbital of the carbonyl substituent, hampering the formation of pre-reactive complexes in the reaction with OH radicals. As a result, CF_3CHO are significantly less reactive toward OH than other organic aldehydes, rendering photolysis to be a particularly crucial atmospheric removal pathway for CF_3CHO .

Table 2-1. Atmospheric OH-initiated degradation mechanisms of representative F-gas precursors leading to CF₃CHO formation.

Compound	atmospheric degradation via OH radicals
HFO-1234ez	
HFE-236fa	
Halon-2301	
HCFC-235fa	
HFC-143a	

Upon photoexcitation, CF₃CHO undergoes several competing dissociation pathways:



As most aldehydes, the principal pathway is the classical Norrish type I cleavage, in which the C–C bond breaks to yield CF₃ and HCO radicals (reaction R2-1a) (Campbell et al., 2021). Notably, accumulating evidence has revealed the existence of a competing molecular channel, producing CHF₃ and CO (reaction R2-1b) (Campbell et al., 2021; Thomson et al., 2025; Van Hoomissen et al., 2025), analogous to molecular channels observed in other fluorinated gases and aldehydes (Atkinson et al., 2004; Jubb et al., 2015; McGillen et al., 2020b). CHF₃ (fluoroform, also known as HFC-23) has been known to be one of the most potent greenhouse gases, with an atmospheric lifetime of ~228 years and a 100-year global warming potential (GWP) of ~14700 (WMO, 2022). This means that even a very

small branching ratio toward CHF₃, when combined with the global abundance of fluorinated precursors, could translate into a disproportionately large climate burden.

Between 2015 and 2022, top-down atmospheric studies consistently reported global HFC-23 emissions exceeding industrially reported values by approximately 10–14 Gg yr⁻¹. (Stanley et al., 2020) highlighted this discrepancy, which has since been reaffirmed in the most recent UNEP assessment (Montzka et al., 2024). This suggests the presence of additional, unreported sources of HFC-23, possibly including indirect chemical pathways such as the photolysis of CF₃CHO.

Spanning studies over nearly 70 years, numerous experimental approaches have been employed to investigate the photolysis of CF₃CHO with varying irradiation conditions. Different types of light sources have been applied, ranging from pulsed lasers at discrete wavelengths (248, 266, 281, 308 nm) (Chiappero et al., 2006; Thomson et al., 2025; Van Hoomissen et al., 2025), to filtered arc lamps at 313 nm (Dodd and Smith, 1957; Pearce and Whytock, 1971), to low-pressure mercury and fluorescent lamps at 254 nm (Chiappero et al., 2006; Sulbaek Andersen et al., 2023), and to broadband UV sources covering 290–400 nm (Sellevåg et al., 2004; Sulbaek Andersen and Nielsen, 2022). Collectively, these studies have established the fundamental photochemical pathways of CF₃CHO and provided valuable information. However, substantial discrepancies remain in these reported quantum yields, particularly with regard to the product of CHF₃.

Measurements of the total quantum yield of CF₃CHO photolysis, $\Phi(\text{total})$, reported in the literature generally indicate an increase with photon energy in single-wavelength experiments, approaching unity at shorter wavelengths. In contrast, studies relying on broadband UV irradiation offered systematically lower effective quantum yields (Sellevåg et al., 2004; Sulbaek Andersen and Nielsen, 2022). Since broadband measurement is currently the only available parametric characterization approach for CF₃CHO photolysis, this correspondingly leads to a large uncertainty in the photolysis rate of CF₃CHO. The detailed features mentioned here can be found in Section 2.3.2 below.

Significant inconsistencies are also evident in reported CHF₃ product yields, $\Phi(\text{CHF}_3)$. While several single-wavelength studies at shorter wavelengths ($\lambda \leq 290$ nm) show reasonable agreement, reported

yields at longer wavelengths within the actinic range, particularly near 308 and 313 nm, vary by orders of magnitude across different studies. In some cases, CHF₃ formation is reported at levels of 10⁻², whereas other studies suggest yields as low as 10⁻⁴ or even below detection limits. The detailed features mentioned here can be found in Section 2.3.3 below. These large divergencies highlight both the experimental challenges associated with quantifying minor photolysis products and the sensitivity of CHF₃ formation to irradiation conditions and experimental methodology. Given that the absorption cross section of CF₃CHO extends well into the actinic range, potentially allowing efficient photolysis, even minor errors in CHF₃ production could significantly affect the assessment of the climate impact of HFO and other CF₃CHO precursors.

Accordingly, this chapter has two major objectives: first, to provide quantitative laboratory data on the $\Phi(\text{total})$ and $\Phi(\text{CHF}_3)$ under atmospherically relevant conditions (both tropospheric and stratospheric wavelengths) through a series of single-wavelength and broadband UV experiments; second, to assess the indirect GWP of CF₃CHO and, further, its fluorinated precursors by parameterizing these newly provided data and then applying existing Stern-Volmer analysis combined with other oxidation pathways such as OH and HO₂.

2.2 Methodology

2.2.1 Synthesis and chemicals

All reactant chemicals, except CF₃CHO, were obtained from commercial suppliers: CO ($\geq 99.997\%$, Alphagaz), N₂ ($\geq 99.9999\%$, Alphagaz), purified air ($\geq 99.9999\%$, Alphagaz), trifluoromethane (CHF₃, $\geq 99.99\%$, ABCR), iodomethane (CH₃I, $\geq 99.5\%$, Sigma Aldrich), nitric acid (HNO₃, $\geq 69\%$, Sigma Aldrich), 1,3,5-trimethylbenzene ($\geq 97\%$, TCI).

CF₃CHO is not commercially available and therefore was synthesized in-house via the dehydration of its stable and commercially available hydrate form, CF₃CH(OH)₂ (75% in water), the following method was adapted from previous studies (Figure 2-1) (Berney, 1969; Ram Reddy et al., 2002; Sulbaek Andersen and Nielsen, 2022; Thomson et al., 2025).

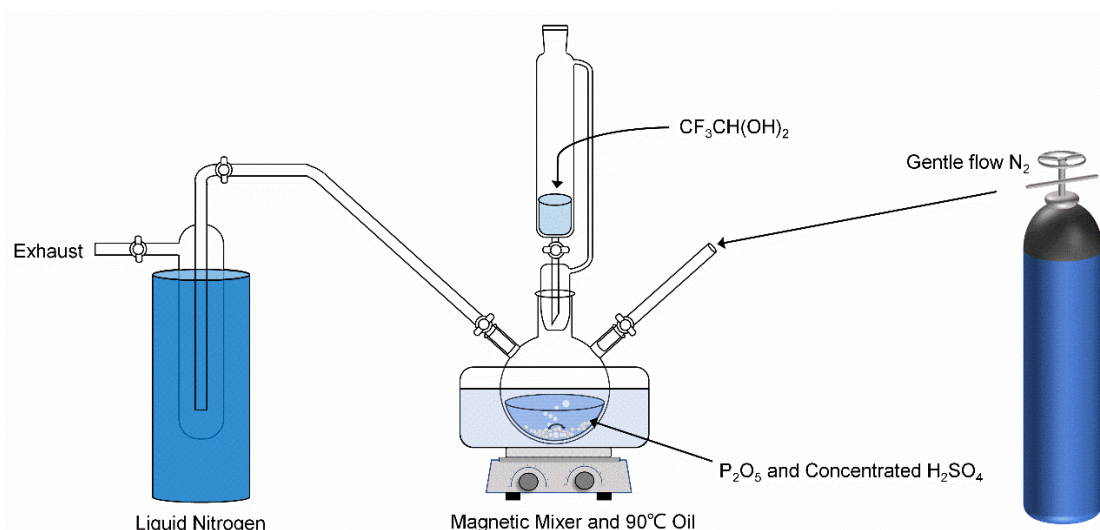


Figure 2-1. Schematic of the synthesis of CF_3CHO sample by dehydration of its commercial monohydrate.

The synthesis was carried out under strictly dry and inert conditions to prevent premature hydrolysis and decomposition. In a typical preparation, phosphorus pentoxide (P_2O_5) was dispersed in concentrated sulfuric acid (H_2SO_4) within a three-neck round bottom flask equipped with stopcock valves and magnetic stirring. The mixture was stirred and heated to $\sim 90^\circ\text{C}$ in an oil bath to form a viscous dehydrating medium. Dry nitrogen was continuously purged through the system via a dedicated gas inlet to exclude any interference or byproducts, e.g., moisture (H_2O) and carbon dioxide (CO_2). Once the medium was thermally equilibrated, $\text{CF}_3\text{CH}(\text{OH})_2$ was slowly added dropwise through a pressure-equalized dropping funnel. Controlled addition was essential to prevent over-foaming and to maintain reaction stability. As dehydration proceeded, gaseous CF_3CHO was liberated and carried by the nitrogen stream to a downstream glass trap submerged in liquid nitrogen (-196°C), where it was condensed.

After the reaction had finished, the cold trap containing solid CF_3CHO was sealed while immersed in liquid nitrogen, and the system was evacuated and degassed by multiple freeze-pump-thaw cycles. The purified CF_3CHO was transferred into a pre-dried glass bulb and stored under nitrogen in dark conditions at ambient temperature. Purity and stability were routinely checked using FTIR spectroscopy, showing no observable hydrolytic, oxidative or photolytic degradation under dark and dry conditions for at least several months.

2.2.2 Single wavelength measurement

Single-wavelength photolysis experiments were carried out using the purpose-built Long-Axis Reactor for KINetic studies (LARKIN, see a photograph in Figure 2-2). A full schematic of the LARKIN apparatus is shown in Figure 2-4. LARKIN is a jacketed cylindrical Pyrex reactor approximately 1 m in length with a total internal volume of $\sim 4055 \text{ cm}^3$. The reactor was equipped with Suprasil[®] windows on each end of the reactor ensuring high UV transmission from 200 nm and throughout the actinic range, and a 0° reflector centered on 300 nm was positioned on the exit side to maximize photolysis rates. The reactor temperature was regulated at $298 \pm 2 \text{ K}$ by circulating a cryostat-controlled cooling/heating fluid. To prevent condensation, all window assemblies were evacuated. During the experiment, the gaseous content was periodically mixed using an all-Teflon diaphragm pump (mixing for 1 minute every 30 minutes) to maintain homogeneity and prevent localized accumulation of reactive species.

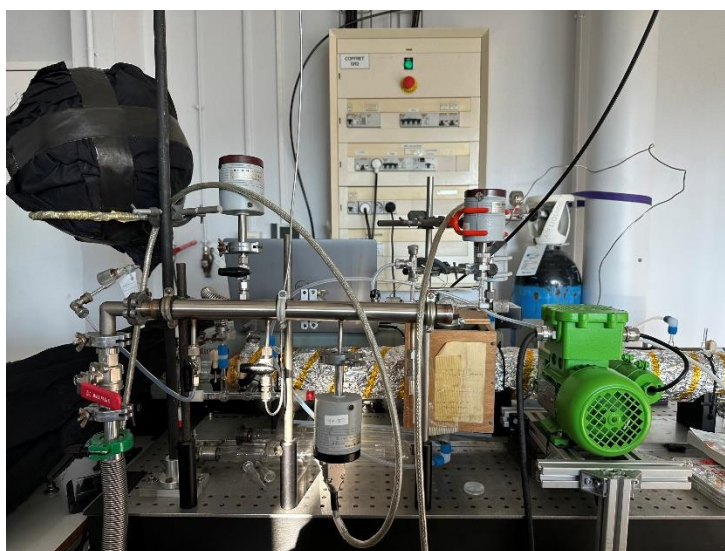


Figure 2-2. Photograph of the LARKIN experimental setup used for quantum yield and relative rate measurements. The image shows the photolysis reactor (centre), associated gas handling lines, pressure regulation components, and circulation pump (green, right). Instrumentation for detection (e.g., FTIR, SPIRIT) is located externally and not shown in this image.

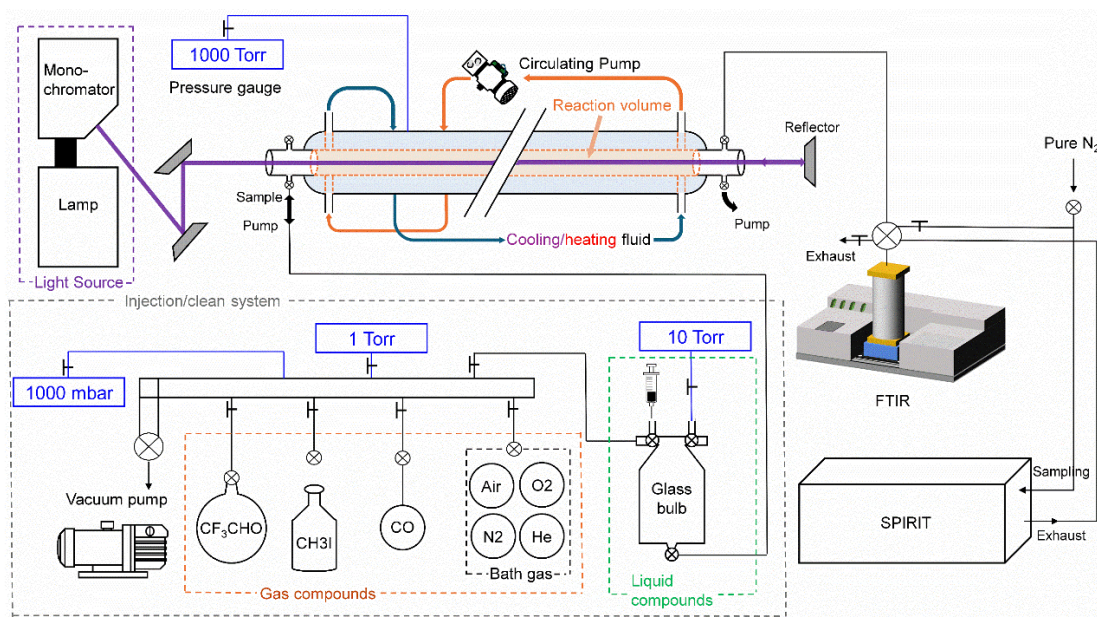


Figure 2-3. Schematic of the LARKIN experimental apparatus.

The injection/vacuum system includes a stainless-steel manifold and a 596 cm³ glass bulb, where liquid or gaseous samples were introduced under strictly controlled pressure conditions, monitored using pressure gauges (MKS Baratron) with operational ranges of 1000 mbar, 1 Torr and 10 Torr. A 1000 Torr pressure gauge was used to track the total pressure within the reaction volume to monitor possible leaks in the apparatus during the photolysis phase. Prior to each experiment, the reactor was evacuated using a dry scroll pump and purged repeatedly with zero air or dry nitrogen to ensure cleanliness.

For photolysis, LARKIN is coupled to either a KrF excimer laser ($\lambda = 248$ nm, Coherent COMPexPro 110) or a custom-built tunable UV lamp (HORIBA) coupled with a monochromator depending on the nominal wavelength of interest (see Figure 2-4) This setup allowed narrowband UV outputs to be selected with high spectral resolution. Light intensity and spectral distribution were monitored using a calibrated spectrophotometer with representative spectra for selected wavelengths presented in Figure 2-12 in Section 2.3.2.

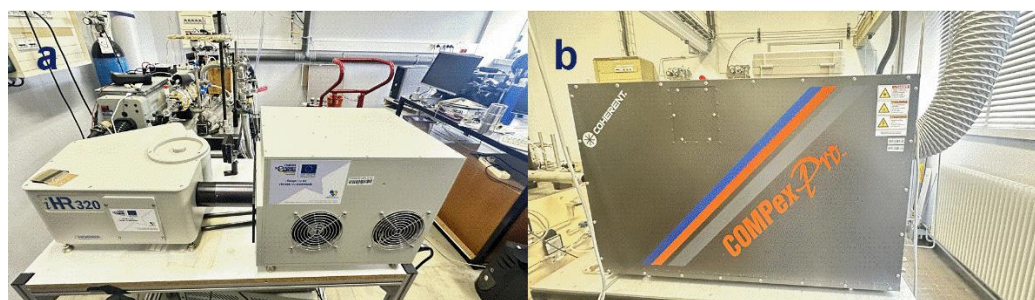


Figure 2-4. Photographs of the light sources used in this study. *Panel a:* Broadband UV lamp coupled with a monochromator for wavelength-tunable actinic irradiation. *Panel b:* KrF excimer laser (248 nm) employed for photolysis experiments in the UV-C region.

Two complementary analytical techniques were employed to monitor reactants and products in the experiments: Fourier-transform infrared spectroscopy (Nicolet 550 Magna FTIR spectrometer) and the SPIRIT instrument (SPectromètre Infra-Rouge In situ Troposphérique). FTIR is coupled to a White-type multi-pass mirror cell (2 L volume and 10 m optical path length) and served as the primary method for *in situ* monitoring of photolytic reactants (e.g., CF_3CHO and reference compounds) and other photoproducts (e.g., CF_2O). IR spectra were recorded every ten minutes, derived from 100 co-added interferograms with a spectral resolution of 0.25 cm^{-1} . Prior to measurement, the gaseous contents were homogenized by circulating for one minute using an all-Teflon diaphragm pump.

Following photolysis, the light source was switched off, and the reactor was connected to a home-built instrument, SPIRIT for the detection of CHF_3 . SPIRIT is a custom made continuous-wave quantum cascade laser (CW-QCL) infrared spectrometer that has been previously employed in field observation for detecting greenhouse gases (e.g., CH_4 , CO_2 , N_2O) (Guimbaud et al., 2016, 2011). Its detection limit reaches ppb precision, and its architecture is optimized for high selectivity and spectral resolution in the mid-infrared region (e.g., 1262 cm^{-1}), where CHF_3 presents a distinct and strong vibrational band. The instrument employs a single-mode distributed feedback quantum cascade laser (DFB-QCL) in CW mode, thermoelectrically stabilized via a Peltier cooler to ensure mode stability and minimal frequency drift. The laser beam is directed into a patented multipass optical absorption cell (French Patent FR2889599), where it interacts with sample gases over an adjustable effective pathlength up to 84 meters.

A schematic of SPIRIT is illustrated in Figure 2-5. Laser emission is modulated by a sawtooth current ramp and synchronized via a dedicated acquisition module. A beam splitter divides the signal into two optical paths—one to a measurement detector, the other to a reference detector equipped with a Fabry–Pérot etalon for internal frequency calibration. Laser tuning is achieved by varying injection current and temperature, offering flexible spectral coverage in the range 1255–1265 cm^{-1} . The measurement procedure involves sampling gaseous products directly into the optical cell at ambient pressure. A liquid nitrogen-cooled MCT (mercury cadmium telluride) detector ensures low noise and rapid response.

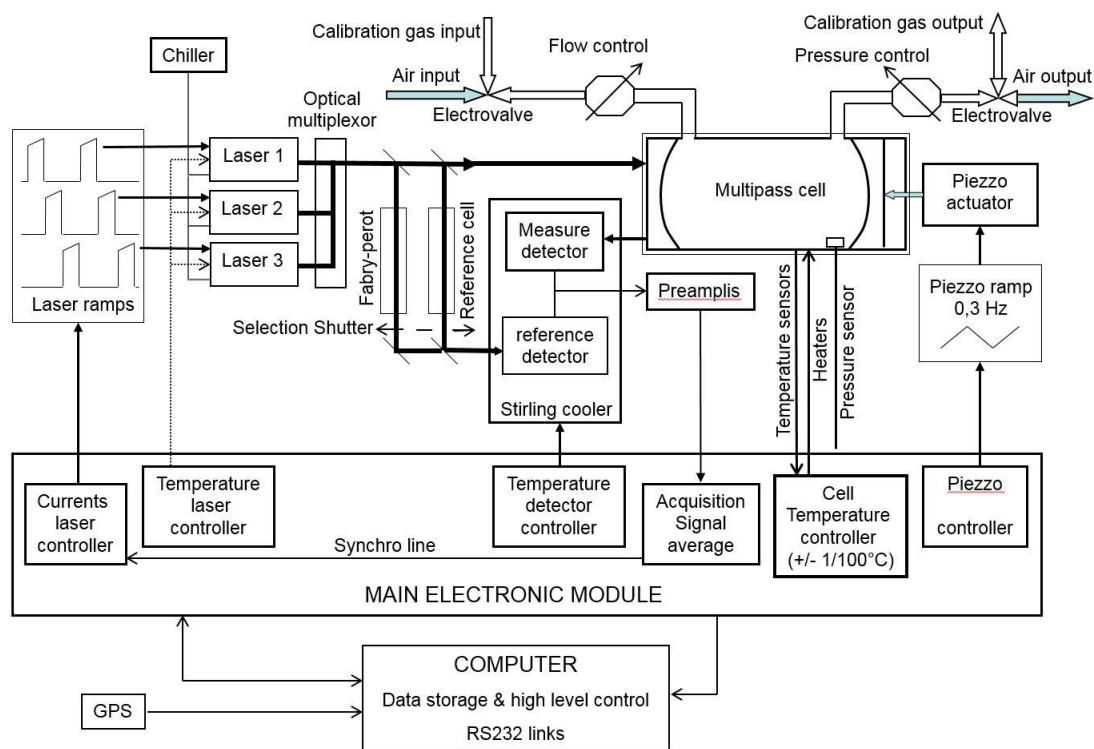


Figure 2-5. Schematics of the instrument principle of SPIRIT.

Calibration of SPIRIT on CHF_3 signals was carried out using internally prepared dilute gas mixtures, which were made by mixing a small partial pressure of standard CHF_3 gas with high-purity zero air. The mixing ratio was determined by adding a known pressure of CHF_3 measured using a 1 Torr Baratron pressure gauge and adding the balance of zero air which was quantified using a 10,000 Torr Baratron pressure gauge. To evaluate reproducibility, several independent calibration mixtures were

prepared, and the results demonstrated agreement to better than 3% (refer to Figure A2-1). We observed a minor interference on the CHF_3 absorption line caused by the nearly absorption band of CF_3CHO . Therefore, the measured CHF_3 signal was corrected according to the quantified $[\text{CF}_3\text{CHO}]$ derived from FTIR measurements (refer to Figure A2-2).

2.2.3 Broadband UV measurement

Broadband UV experiments were conducted in a large outdoor atmospheric simulation chamber named HELIOS (ACTRIS exploratory platform, Orléans, France). HELIOS is the largest outdoor chamber in France and is integrated within the pan-European research infrastructure. A detailed description of the facility is available elsewhere (Ren et al., 2017), so only a brief summary of features specific to this work is given here. A photograph is provided in Figure 2-6 and a schematic is given in Figure 2-7.

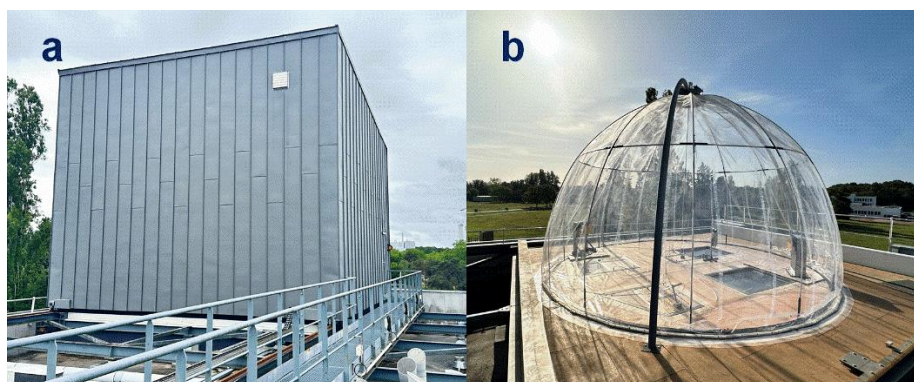


Figure 2-6. Photographs of the external structure of the HELIOS chamber facility. *Panel a:* Protective housing closed for indoor photolysis experiments under artificial UV light. *Panel b:* Protective housing opened to allow exposure to natural sunlight for ambient photolysis experiments.

The reactor is a hemispherical enclosure constructed from FEP Teflon film and housed within a metallic shelter. Forty-nine 160 W fluorescent UV lamps (Philips/iSOLde CLEO Advantage F71T12) are mounted inside the metallic shell, enabling experiments to be carried out under either natural sunlight or artificial irradiation. In this study, CF_3CHO photolysis was investigated under both conditions, with

spectral distributions and intensities monitored using a calibrated photometer. Each experiment began with a clean chamber, achieved through extended flushing with zero air supplemented by periodic physical and chemical cleaning processes. During experiments, a continuous flow of zero air (5 L min^{-1}) was introduced to maintain a slight positive pressure and thereby prevent external air intrusion. As a result, the internal gas mixture was subject to continuous dilution, with the dilution rate calculated using SF_6 as a tracer.

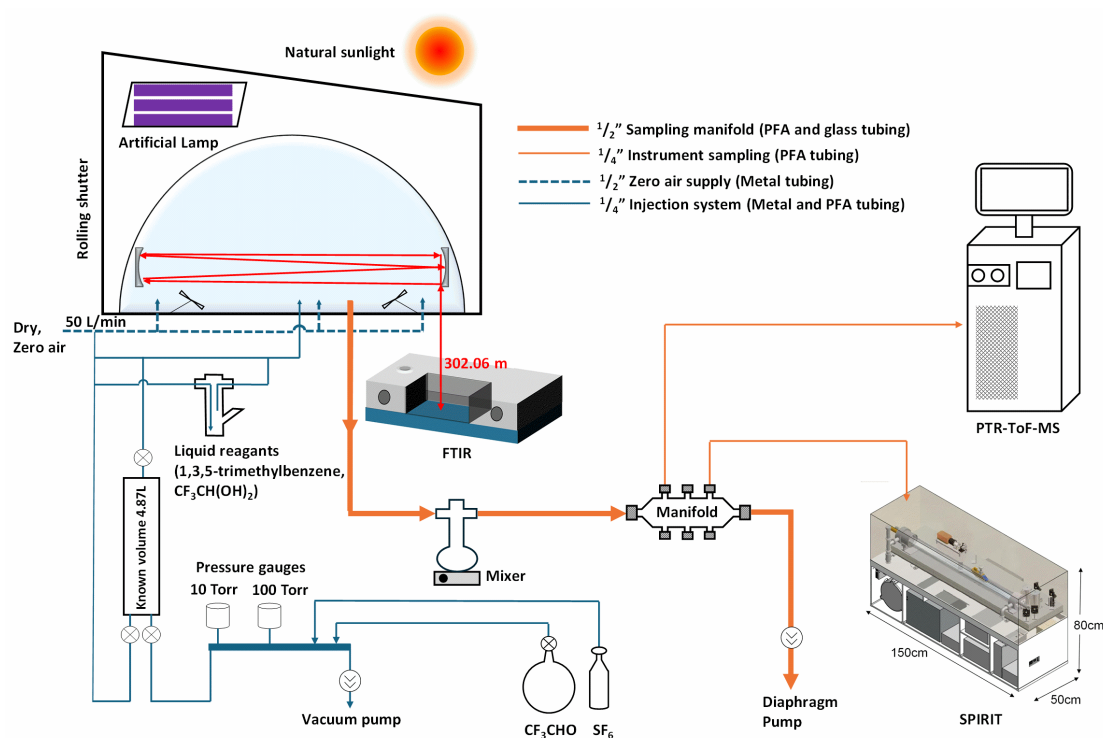


Figure 2-7. Schematic of the HELIOS chamber facilities.

Following these preparations, a known amount of CF_3CHO was injected into the chamber and homogenized within $\sim 90 \text{ s}$ by two circulation fans. Photolysis was then initiated by exposing the chamber either to natural sunlight or to the artificial UV irradiation with typical photolysis time of $\sim 300 \text{ minutes}$. PTR-ToF-MS (PTR-8000, IONICON) was employed in O_2^+ mode with a drift tube voltage of 600 V to continuously monitor CF_3CHO for at least one hour in the dark, allowing background loss rates to be characterized (due to factors such as dilution, wall loss or instrumental stability). O_2^+ is a more intense chemical ionization method that promotes extensive fragmentation of analytes but is capable of detecting compounds that are not detectable using H_3O^+ or NH_4^+ . We found it to be well-

suited for this purpose. CF₃CHO underwent fragmentation to produce a dominant CHO⁺ fragment (*m/z* = 29.003), which was therefore used for the CF₃CHO monitoring. Gas mixtures were monitored *in situ* in parallel by a Bruker Vertex 70 FTIR spectrometer in the mid-IR (4000–700 cm⁻¹), operating at a resolution of 1 cm⁻¹ with a 302.6 m optical path length. Each spectrum was obtained by co-adding 250 interferograms over a 6 min interval.

2.2.4 Quantum yield

Absolute photolysis quantum yields of CF₃CHO were determined at discrete wavelengths using a reference compound with well-characterized quantum yields and absorption cross section. For a given wavelength, the photolysis quantum yield was derived using the following Equation 2-1:

$$\Phi(\text{total}) = \Phi(\text{Ref}) \times \frac{J(\text{CF}_3\text{CHO})}{J(\text{Ref})} \times \frac{\sigma(\text{Ref})}{\sigma(\text{CF}_3\text{CHO})} \quad \text{Equation 2 – 1}$$

where $\Phi(\text{CF}_3\text{CHO})$ and $\Phi(\text{Ref})$ are quantum yields of CF₃CHO and reference compound respectively, and $\sigma(\text{CF}_3\text{CHO})$ and $\sigma(\text{Ref})$ are their respective absorption cross-sections. The term of $J(\text{CF}_3\text{CHO})/J(\text{Ref})$ was based on the relative photolysis rate coefficient (*J*) between CF₃CHO and reference, which was determined by monitoring the relative decay of CF₃CHO and reference compound under identical experimental conditions. It's noted that in our analysis, instead of observing $\Delta[\text{CF}_3\text{CHO}]$, we used the sum of $\Delta[\text{CF}_2\text{O}]$ and $\Delta[\text{CHF}_3]$ as a metric of photolytic CF₃CHO loss, yielding Equation 2-2:

$$\ln\left(\frac{[\text{CF}_3\text{CHO}]_0}{[\text{CF}_3\text{CHO}]_0 - \Delta[\text{CF}_2\text{O}]_t - \Delta[\text{CHF}_3]_t}\right) = \frac{J(\text{CF}_3\text{CHO})}{J(\text{Ref})} \ln\left(\frac{[\text{Ref}]_0}{[\text{Ref}]_t}\right) \quad \text{Equation 2 – 2}$$

where $[\text{CF}_3\text{CHO}]_0$ and $[\text{Ref}]_0$ are the initial concentrations of CF₃CHO and reference compound respectively, $[\text{CF}_3\text{CHO}]_t$, $[\text{Ref}]_t$, $\Delta[\text{CF}_2\text{O}]_t$ and $\Delta[\text{CHF}_3]_t$ are the concentrations at time *t*. The parameters $J(\text{CF}_3\text{CHO})$ and $J(\text{Ref})$ correspond to the first-order rate coefficients for photodissociation reactions of CF₃CHO and reference compound respectively. In this expression, the actual photolytic loss of CF₃CHO is represented by the sum of $\Delta[\text{CF}_2\text{O}]_t$ and $\Delta[\text{CHF}_3]_t$, from which we therefore obtain $[\text{CF}_3\text{CHO}]_t = [\text{CF}_3\text{CHO}]_0 - \Delta[\text{CF}_2\text{O}]_t - \Delta[\text{CHF}_3]_t$. The reason why we used this adopted expression is because the

presence of an equilibrium reaction between CF_3CHO and its monohydrate form, $\text{CF}_3\text{CH}(\text{OH})_2$ in the system. Over a long photolysis duration, this could be problematic to quantification of photolytic loss of CF_3CHO . A more detailed discussion about this hydration process is presented in the next Section 2.3.

Product yields of CHF_3 were determined from independent photolysis experiments, in which no chemical actinometer was used. The molar yield, $Y(\text{CHF}_3)$ was derived using Equation 2-3:

$$Y(\text{CHF}_3) = \frac{\Delta[\text{CHF}_3]_t}{\Delta[\text{CF}_2\text{O}]_t + \Delta[\text{CHF}_3]_t} \quad \text{Equation 2 - 3}$$

where $\Delta[\text{CHF}_3]_t$ and $\Delta[\text{CF}_2\text{O}]_t$ are the measured concentrations of CHF_3 and CF_2O at time t , respectively. The sum of $\Delta[\text{CF}_2\text{O}]_t + \Delta[\text{CHF}_3]_t$ represents the photolytic loss of CF_3CHO as described above. The product yield was then calculated by multiplying the molar yield, $Y(\text{CHF}_3)$ by the total quantum yield of CF_3CHO , $\Phi(\text{total})$ at each corresponding wavelength:

$$\phi_\lambda(\text{CHF}_3) = Y_\lambda(\text{CHF}_3) \times \phi_\lambda(\text{total}) \quad \text{Equation 2 - 4}$$

2.2.5 Error analysis

In this section, the quoted uncertainties for the photolysis measurements at each wavelength are quantified, and the formulae applied to calculate the uncertainties on the quantum yield determination are provided. Overall, uncertainties stem primarily from absorption cross sections, calibration methods, and data processing steps:

(i) Absorption cross-section

Each compound involved in the calculation, i.e., CF_3CHO , CF_2O , and CHF_3 accounted for approximately 5% uncertainty from previous reported absorption cross-section values.

(ii) IR spectral overlap and manual subtraction

The subtraction of overlapping IR spectral features, particularly for complex spectra, introduces uncertainties ranging from 5% to 15%, depending on the difficulties of manual subtraction.

(iii) SPIRIT instrument calibration (only applied in $\Phi(\text{CHF}_3)$)

An estimated 10% uncertainty originates from the SPIRIT calibrations, reflecting accuracy of the pressure-controlled dilution used to prepare the CHF_3 standard mixtures.

These uncertainties are combined using the general formula for multiplicative and divisive error propagation (Equation 2-5):

$$\text{Uncertainty} = \phi \times \sqrt{\sigma_1^2 + \sigma_2^2 + \dots} \quad \text{Equation 2 – 5}$$

where *Uncertainty* denotes the total uncertainty associated with the quantum yield, incorporating contributions from various experimental factors. ϕ represents the measured quantum yield of CF_3CHO or CHF_3 . The terms $\sigma_1, \sigma_2, \dots$ are the relative uncertainties contributed by individual sources mentioned above in this section. The square root of the sum of the squares accounts for error propagation in multiplicative and divisive operations, under the assumption that all sources of uncertainty are independent and can be combined in quadrature.

2.3 Results and discussion

2.3.1 Chemical consideration

The single-wavelength experiments conducted in LARKIN were performed in high-purity zero air as the bath gas, into which CF_3CHO , a reference compound (when needed), and CO (as a radical scavenger) were introduced sequentially. The pressure was adjusted to slightly above 1 bar. Input concentrations and detailed conditions for each experiment are provided in Table A2-1 and Table A2-2. CO was found to be highly effective not only in converting CF_3O radical (Meller and Moortgat, 1997) but also in suppressing the HO_x budget in the system (Atkinson et al., 2004; Volman, 1996). In previous studies, nitric oxide (NO) was commonly employed to suppress secondary radical chemistry during CF_3CHO photolysis, by capturing CF_3 , HCO and H radicals to form CF_3NO and HNO as quantifiable products (Sulbaek Andersen et al., 2023; Sulbaek Andersen and Nielsen, 2022; Thomson et al., 2025; Van Hoomissen et al., 2025). However, NO could generate a suite of photolabile oxidant reservoirs,

even under low O_2 conditions, including CF_3ONO , NO_2 , O_3 , $HONO$ and HO_2NO_2 , which can possibly introduce additional CF_3CHO loss through reactions with CF_3O , OH , HO_2 , $O(^3P)$, or $O(^1D)$. In practice, we noted that earlier studies have already reported that during extended photolysis duration, CF_3NO can be photolyzed slowly and then lead to regeneration of CF_3 radicals that could be scavenged by NO again or incidentally react with trace O_2 in the system to form CF_2O (Sulbaek Andersen and Nielsen, 2022; Thomson et al., 2025). By contrast, this study adopted an alternative O_2/CO strategy, by which could effectively convert fluorine reservoirs and direct final photolysis products toward CF_2O , CHF_3 and CO , as the chemical mechanism illustrated in Figure 2-8.

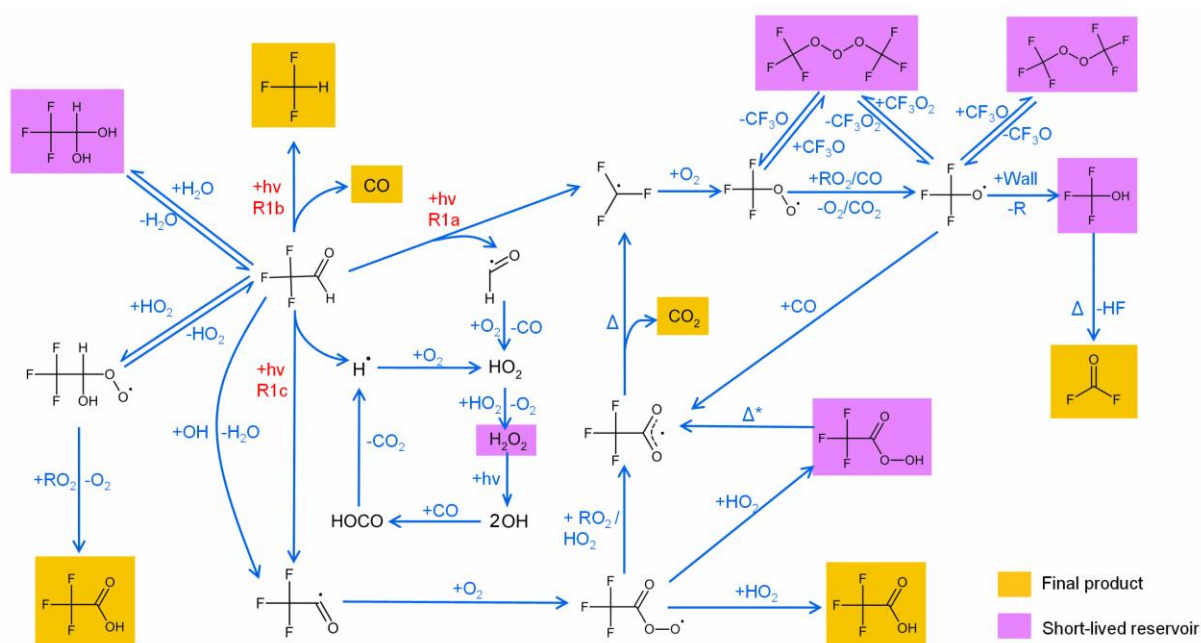


Figure 2-8. The reaction mechanism in this study for the photolysis of CF_3CHO . R1a, R1b, R1c (red marker) denote the three possible photolysis pathways of CF_3CHO .

In Figure 2-8, the dominant photolysis channel of CF_3CHO is the Norrish type I cleavage (channel R1a), producing CF_3 and HCO radicals. CF_3 radicals produced are efficiently trapped by O_2 , and in the presence of CO ultimately yield CF_2O , thereby terminating the reaction chain. Along this route, several short-lived fluorine reservoirs (e.g., $CF_3O_3CF_3$, $CF_3O_2CF_3$ and CF_3OH) are transiently formed and converted into CF_2O over extended photolysis durations (Meller and Moortgat, 1997). After subtracting features for CF_3CHO , $CF_3CH(OH)_2$ and CHF_3 in the IR spectra, no residual absorption bands

were observable in the C–F stretching region (1100–1450 cm^{-1}), confirming CF_2O as the terminal sink. HCO radicals are trapped by O_2 to produce HO_2 that could subsequently undergo self-reaction to form OH . HO_x radicals are considered to be effectively suppressed by the presence of excess CO . We did not observe any IR features attributable to $\text{CF}_3\text{C(O)OH}$, a potential product of the HO_2 reaction, at 1120 or 1830 cm^{-1} , which confirmed this point. The R1c pathway, leading to CF_3CO and H , is considered to be a very minor channel under actinic conditions. No experimental evidence has been obtained to date for its occurrence and even if CF_3CO were formed, it would be decomposed to CF_3 or proceed via $\text{CF}_3\text{C(O)O}_2$ to ultimately generate CF_3 , which in turn is converted into CF_2O (Wallington et al., 1994).

In preliminary experiments at 300 nm, we observed $\sim 30\%$ reduction in $\Phi(\text{CHF}_3)$ in the absence of CO , which we attribute to unwanted loss processes of CF_3CHO , such as side reactions of OH , HO_2 , and/or CF_3O radicals that do not lead to CHF_3 formation.

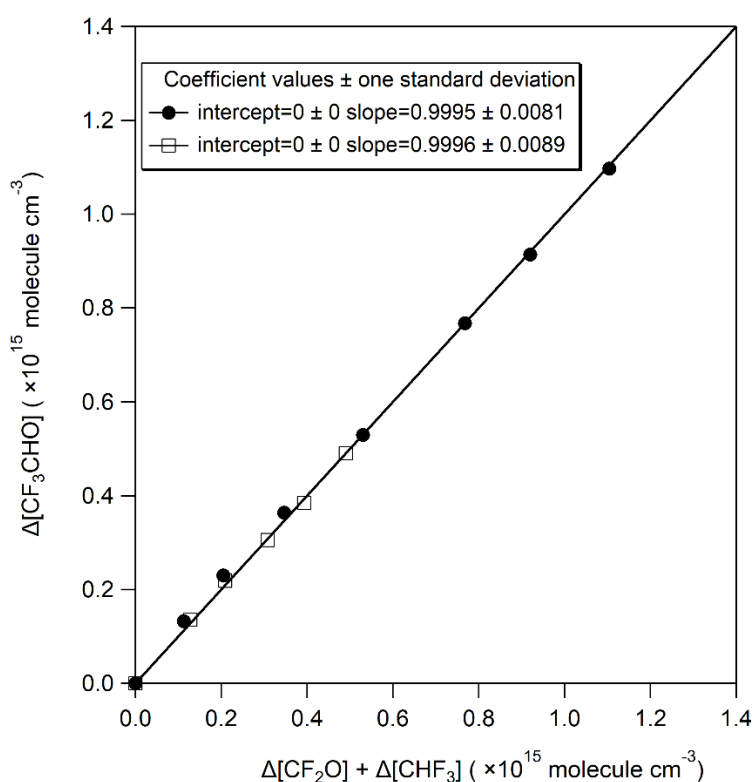


Figure 2-9. Linear relationship between the photolytic loss of CF_3CHO and the product formation of CF_2O and CHF_3 for two independent experiments at 248 nm. Linear fits constrained to pass through origin give slopes indistinguishable from unity, demonstrating the relation $\Delta[\text{CF}_3\text{CHO}] = \Delta[\text{CF}_2\text{O}] + \Delta[\text{CHF}_3]$ within experimental uncertainty.

For the determination of $\Phi(\text{total})$ and $\Phi(\text{CHF}_3)$, we used $(\Delta[\text{CF}_2\text{O}] + \Delta[\text{CHF}_3])$ as the photolysis proxy rather than directly monitoring $\Delta[\text{CF}_3\text{CHO}]$, as described in Section 2.2.4. This approach was necessary because, in the single-wavelength experiments, the low photon flux from the tuneable lamp ($\lambda \neq 248$ nm) resulted in prolonged photolysis time (often ≥ 24 h), by which time a small fraction of CF_3CHO ($\sim 4\%$ over 27 h) was found to be converted into its monohydrate form, $\text{CF}_3\text{CH}(\text{OH})_2$. Given the magnitude of photolytic conversion of CF_3CHO and the low yields of CHF_3 in the actinic range, this side loss was sufficient to introduce uncertainties into the quantum yield calculations. By contrast, no measurable losses of CF_2O and CHF_3 were observed at the photolysis wavelengths investigated, making them reliable indicators for the fluorine sink in the system. It is noted that in laser experiments ($\lambda = 248$ nm), this hydration is typically not a major concern as the high photon flux significantly shortened the photolysis time. This is further confirmed by plotting $\Delta[\text{CF}_3\text{CHO}]$ versus $(\Delta[\text{CF}_2\text{O}] + \Delta[\text{CHF}_3])$, where the fitted slopes are indistinguishable from 1 (Figure 2-9).

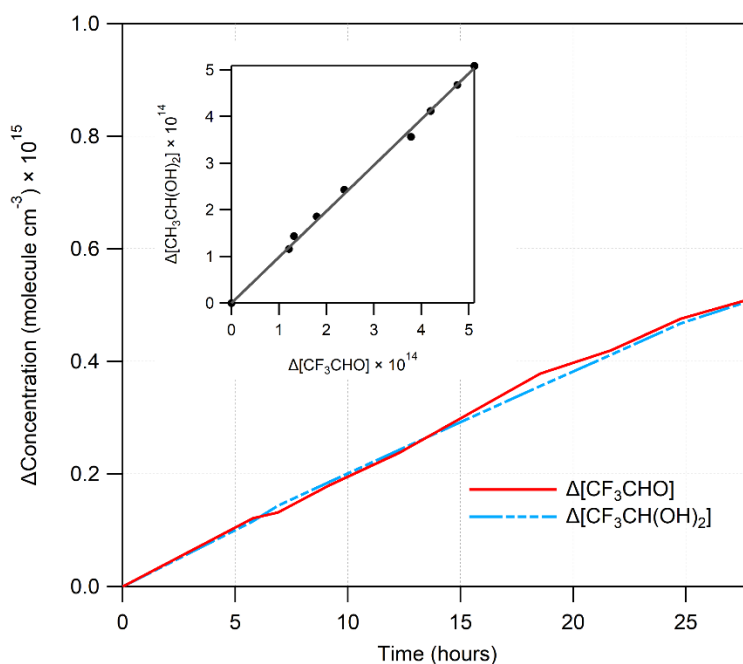


Figure 2-10. Dark experiment in the LARKIN photoreactor: time-series decay of CF_3CHO (red line) and the formation of its monohydrate, $\text{CF}_3\text{CH}(\text{OH})_2$ (blue line), over a course of 27h. An initial mixture of CF_3CHO (red line) and CO was introduced into LARKIN. Approximately 4% of CF_3CHO was lost over the experiment, with a corresponding increase in its monohydrate. The insert shows a linear correlation between the loss of CF_3CHO and formation of $\text{CF}_3\text{CH}(\text{OH})_2$.

As mentioned, in a control experiment shown in Figure 2-10, about 4% of CF_3CHO was found to be converted into $\text{CF}_3\text{CH}(\text{OH})_2$ over 27 h under dark and dry conditions. This is attributed to trace water attached onto Pyrex, metallic fittings, or elastomeric seals that could not be fully removed despite repeated evacuation and zero air flushing. In contrast, when a 72% aqueous solution of $\text{CF}_3\text{CH}(\text{OH})_2$ was vaporized into a 10 L darkened, glass bulb, rapid dehydration was observed, with ~95% of the hydrate reverting to CF_3CHO within 30 min. Such efficient dehydration points to a surface-catalyzed process occurring on the walls, which persists even under humid conditions. To further test this, $\text{CF}_3\text{CH}(\text{OH})_2$ was introduced into the large PFA film HELIOS chamber, where we found, after accounting for dilution, no measurable loss of $\text{CF}_3\text{CH}(\text{OH})_2$ and accumulation of CF_3CHO were detected over a monitoring period of ~320 minutes. These findings are aligned with observations reported previously by (Nielsen et al., 2025; Sulbaek Andersen et al., 2006) and reinforce the conclusion that, this equilibrium reaction between CF_3CHO and $\text{CF}_3\text{CH}(\text{OH})_2$ lies overwhelmingly toward the aldehyde as mediated by catalytic walls. Therefore, the gas-phase concentration of the hydrate remains negligible at any given time for our single-wavelength experiments where we have catalytic surfaces.

2.3.2 Quantum yield of CF_3CHO

In CF_3CHO actinometry experiments, a chemical actinometer with a well-characterized quantum yield and absorption cross-section was employed together with CF_3CHO and CO in the photolysis experiments. In previous studies, acetaldehyde (CH_3CHO) has commonly been used as the reference for $\Phi(\text{total})$ determination (Chiappero et al., 2006; Sulbaek Andersen et al., 2023; Sulbaek Andersen and Nielsen, 2022). However, we noted that small uncertainties remain in both its reported quantum yields and absorption cross-sections, with discrepancies even between the current IUPAC and JPL recommendations (Burkholder et al., 2019; IUPAC, 2025). In addition, CH_3CHO also undergoes Norrish Type I reaction to produce HCO radicals through photolysis, which could further promote HO_x chemistry in the system. In this study, HNO_3 ($\lambda = 248 \text{ nm}$) and CH_3I ($\lambda = 290\text{--}320 \text{ nm}$) were selected as chemical actinometers owing to their unit quantum yields, well-characterized absorption cross sections, simple dissociation pathways, and favourable detection sensitivity in the FTIR measurements. At each wavelength, the ratio between input concentrations of CF_3CHO and actinometer was carefully

adjusted to match their optical depths (defined as the multiplication of UV absorption cross section and molecular concentration) (Seinfeld, 2016). This minimized systematic bias arising from uneven photon absorption and ensured that the observed relative photolysis rates reflected the intrinsic molecular reactivity rather than photon availability. Figure 2-11 presents the relative rate plots for all measured wavelengths.

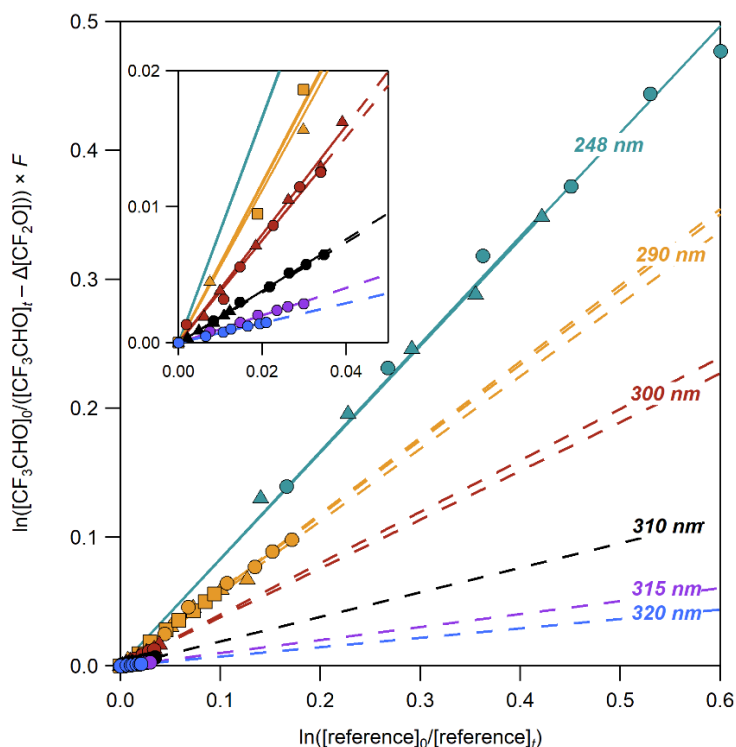


Figure 2-11. All experimentally determined relative rate plots at selected wavelengths (248, 290, 300, 310, 315 and 320 nm). Solid and dashed lines denote linear regressions and extrapolated fits respectively. Photolytic losses of CF_3CHO were derived from the CHF_3 and CF_2O production (see text above). For comparison, photolytic losses of CF_3CHO were additionally normalized using a correction factor $F = \Phi_{\lambda, \text{CH}_3\text{I}} \times \sigma_{\lambda, \text{CH}_3\text{I}} / \sigma_{\lambda, \text{CF}_3\text{CHO}}$, accounting for the absorption cross-section and quantum yield of reference.

High precision, linearity and reproducibility were observed across independent experiments at each wavelength. For the measurements at 248 nm, performed using an excimer laser beam, relatively high photolytic conversions were achieved for both CF_3CHO (>10% of starting material) and the actinometer (>40% of starting material). In contrast, experiments conducted at longer wavelengths

(e.g., 300–320 nm) using tunable lamps exhibited lower photolytic conversions, typically in the range of 2–6% of the initial concentrations. This arises from combined effect of lower photon flux of the tunable light source and the reduced effective quantum yields at longer wavelengths. Despite the smaller conversions under these conditions, the relative rate plots remain highly linear and reproducible. The consistency of the regressions confirms the robustness and reliability of the relative rate analysis.

Results of $\Phi(\text{total})$ are shown in Figure 2-12, and tabulated data together with experimental conditions are provided in Table A2-1. As expected, we found $\Phi(\text{total})$ is highly wavelength-dependent, increasing as the wavelength decreases. According to this, we parameterized the wavelength dependence of $\Phi(\text{total})$ using a simple sigmoidal function, allowing our results to be readily reproduced for future work (see Table 2-2 for parameter details). Compared with literature data, our results show reasonable agreement with those from previous single-wavelength measurements, but are systematically higher than those from broadband UV measurements. The exact origin of this discrepancy must remain uncertain, but one possible explanation is incomplete suppression of secondary radical chemistry under NO_x -assisted conditions, leading to preferential loss of actinometer (CH_3CHO) and thereby biasing $\Phi(\text{total})$. Incidentally, we compared the parameterization of CF_3CHO with that of CH_3CHO , which exhibits a wavelength-dependent photolysis behaviour that is strikingly similar although fluorination red-shifts the absorption maximum by about 10 nm.

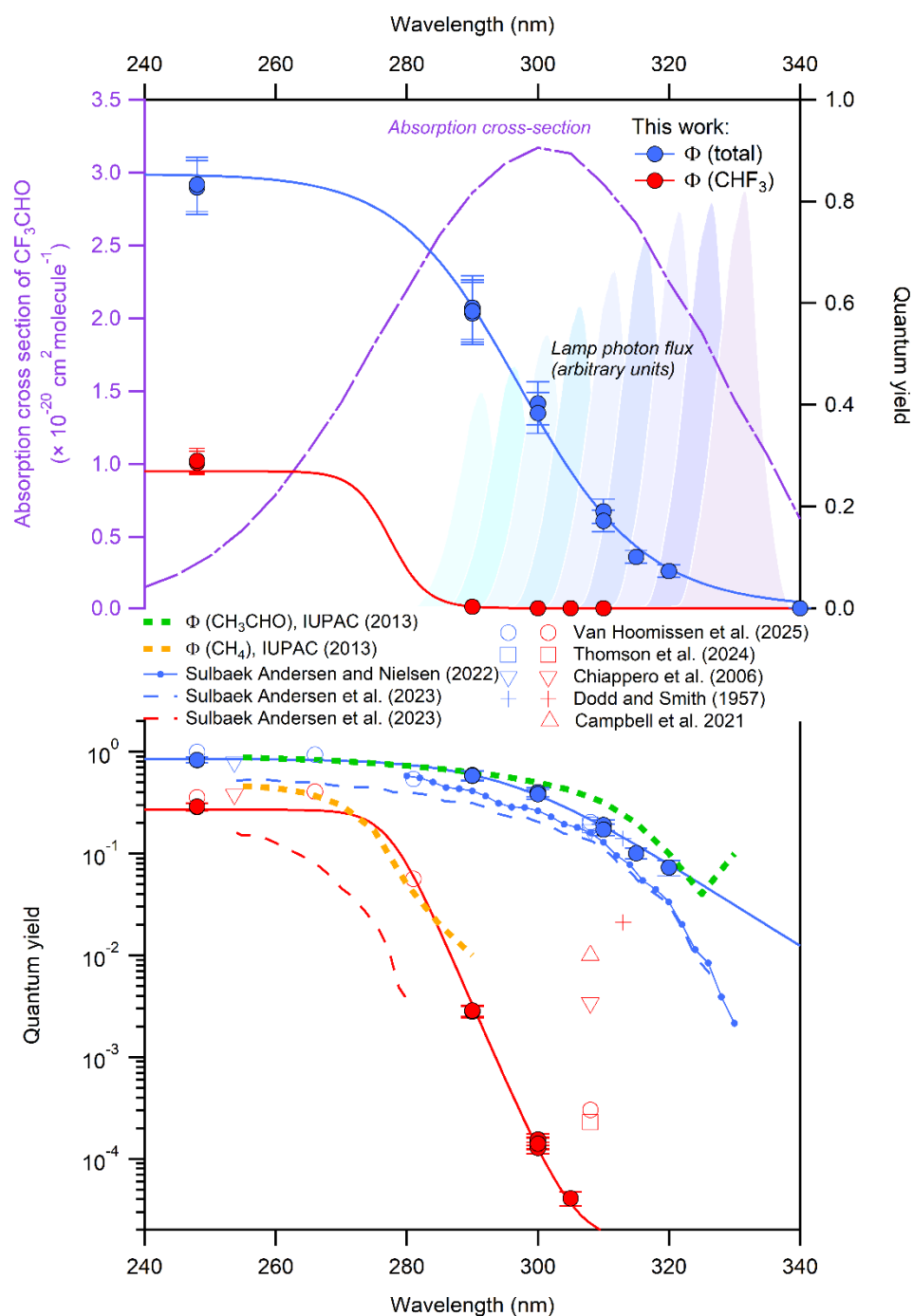


Figure 2-12. Upper panel: photolysis quantum yield of CF_3CHO and product quantum yield of CHF_3 (right axis) from the present study, plotted alongside the absorption cross-section (left axis) from (IUPAC, 2025), all as a function of wavelength. The shaded region represents the relative photon flux from the tunable lamp (arbitrary units). Lower panel: quantum yields on a logarithmic scale for better readability, compared with literature values. Experimental data from this work are shown with solid markers, while literature data are indicated with open symbols (see legend for details).

Table 2-2. Parametrizations of CF₃CHO photolysis quantum yield and CHF₃ formation quantum yield from this work valid over the wavelength range 248 to 340 nm at 298 K and 1 bar. Error denotes $\pm 1\sigma$.

$\Phi(\lambda) = A + (B - A) / \left\{ 1 + \left[\frac{D}{\lambda} \right]^C \right\}$		
Parameter	Φ_{total}	Φ_{CHF_3}
A	$(1.000 \pm 0.001) \times 10^{-6}$	$(1.512 \pm 0.001) \times 10^{-5}$
B	0.853 ± 0.013	0.269 ± 0.008
C	-31.695 ± 1.580	-99.839 ± 21.400
D	297.640 ± 0.526	277.500 ± 0.306

2.3.3 Quantum yield of CHF₃

Figure 2-13 presents all normalized CHF₃ signals obtained from SPIRIT measurements, showing excellent reproducibility and consistency at each wavelength. Obvious CHF₃ formation was observed in the 248–305 nm range, while at longer wavelengths, the signals remained below the SPIRIT detection limit and are therefore not reported here. For measurements in the actinic range, the SPIRIT signal was recorded after prolonged photolysis by switching the gas flow in the photoreactor to the SPIRIT cell. The signal stabilized after ~1 minute, and this plateau region was used for subsequent calculations. Raw data were corrected for interference from CF₃CHO and calibrated with a CHF₃ reference mixture, as described in the Section 2.2.2, enabling accurate quantification as displayed in Figure 2-13. It is evident that after applying these corrections, the CHF₃ signal at 310 nm did not reach a measurable level.

As before, the wavelength-dependent results for $\Phi(\text{CHF}_3)$ are presented in Figure 2-12, which also includes literature values, except for studies that reported no detectable CHF₃ formation such as (Pearce and Whytock, 1971) at 313 nm and (Sellevåg et al., 2004) under broadband UV conditions. Tabulated $\Phi(\text{CHF}_3)$ data together with experimental conditions are summarized in Table A2-2, and a tabulated literature comparison is provided in Table A2-3.

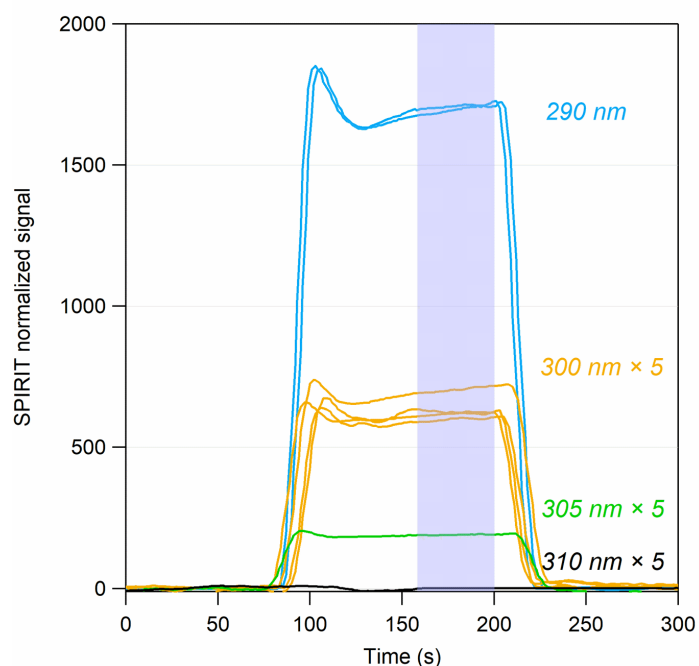


Figure 2-13. Time-series of normalized SPIRIT signals following the UV photolysis at selected wavelengths (290, 300, 305, 310 nm). The normalization expression is $([\text{CHF}_3] - \text{INT}) \times \Delta[\text{CF}_2\text{O}]_t / \Delta[\text{CF}_3\text{CHO}]_t / [\text{CF}_3\text{CHO}]_0$, where INT denote the absorption interference from CF_3CHO . This scaling corrects for differences in photolytic conversion and initial CF_3CHO concentration, allowing for quantitative comparison across conditions. Traces with the same colour denote repeated measurements at the same wavelength. Signals at 300, 305, and 310 nm have been multiplied by a factor of 5 for visibility. The sharp rise and fall indicate the timing of one measurement. The shaded region indicates the time window used to average the signal after reaching a steady signal.

$\Phi(\text{CHF}_3)$ data were again parameterized with a sigmoidal expression with fitting coefficients listed in Table 2-2. At short wavelengths, our parameterization is broadly consistent with earlier single-wavelength studies, although our yields are slightly lower, likely reflecting the negative pressure dependence of $\Phi(\text{CHF}_3)$ as demonstrated by (Van Hoomissen et al., 2025). Conversely, our results are systematically higher than those from (Sulbaek Andersen et al., 2023), where they were likely affected by secondary radical chemistry. In the actinic region, we observed that discrepancies among reported $\Phi(\text{CHF}_3)$ values span more than two orders of magnitude, with our lamp-based results representing the lower bound of this range. We cannot be confident about the exact reasons for these inconsistencies, but we noted that measured $\Phi(\text{CHF}_3)$ is prone to being overestimated under certain

conditions. This involves several factors as follows. First, insufficient scavenging of CF_3 radicals can lead to hydrogen abstraction from CF_3CHO or other hydrogen-containing species, producing additional CHF_3 through the Norrish type I pathway. Second, the negative pressure dependence of $\Phi(\text{CHF}_3)$, as determined by (Van Hoomissen et al., 2025), may exert a stronger influence at actinic wavelengths where yields are intrinsically low. This could help explain the higher values reported by (Campbell et al., 2021) and (Chiappero et al., 2006). Third, the application of pulsed laser sources for measurements in the actinic range, while convenient, raises the concern that two-photon events could disproportionately contribute to $\Phi(\text{CHF}_3)$. At these wavelengths $\Phi(\text{CHF}_3)$ is very low, so occasional two-photon absorption under high photon flux may artificially elevate the measured CHF_3 , whereas at 248 nm, where $\Phi(\text{CHF}_3)$ is large, such effects are negligible. In addition, we compared the parameterized $\Phi(\text{CHF}_3)$ with the CH_4 -forming channel of CH_3CHO photolysis and again found a clear consistency, as both channels drop sharply around 280 nm and remain at low levels across the actinic region.

2.3.4 Chamber experiments

We also performed CF_3CHO photolysis in HELIOS chamber under irradiation from both natural summertime sunlight and artificial actinic lamps. The artificial light simulated tropospheric irradiation, and with all lamps switched on, the photon flux is approximately an order of magnitude higher than that of ambient sunlight. It is worth noting that, although OH radicals can be generated through chain reactions initiated by CF_3CHO photolysis as mentioned in Section 2.2.1, no OH scavenger was applied in these chamber experiments. Firstly, the addition of excess organic compounds was not feasible, as it would cause saturation of IR spectral features and significant spectral overlap. Secondly, CO is not a viable option given the leakage risk in a film-sealed reactor. Thirdly, NO and SO_2 were also considered, but their overlapping spectral absorption with CHF_3 compromised SPIRIT detection. As an alternative, we introduced $4.74 \times 10^{13} \text{ molecules cm}^{-3}$ 1,3,5-trimethylbenzene as a tracer to infer OH concentration. Across several experiments, CF_3CHO was injected at concentrations up to $4.95 \times 10^{14} \text{ molecules cm}^{-3}$, and then subjected to irradiation by natural sunlight or artificial lamps separately. Typical photolysis duration exceeded ~300 minutes. However, the photolytic conversion of CF_3CHO was too small to

permit a reliable determination of quantum yield. The time-series of two representative chamber experiments can be found in Figure A2-3 and Figure A2-4, corresponding to natural and artificial irradiation respectively. In Figure A2-3, no obvious CF₃CHO decay was observed after correcting for dilution loss, with CHF₃ measured below the detection limit. In Figure A2-4, a slight loss of CF₃CHO was observed under enhanced irradiation by artificial light, but still insufficient for quantification analysis of quantum yield. Again, CHF₃ formation was not observed at a quantifiable level. These results are consistent with those previously reported by (Sellevåg et al., 2004), suggesting that, for molecules with low photolysis efficiency, some intrinsic limitations remain in using large-volume chambers. A simple estimate suggests that, if one were to reproduce the photolysis efficiency in small reactors, it would require introducing CF₃CHO at concentrations far beyond practical limits. For this reason, single-wavelength experiments performed in LARKIN are better-suited for the purpose of this study, and chamber experiments are therefore not the focus in this chapter.

2.4 Environmental implications

The new measurements obtained in this study enable us to assess the broader environmental implications of CHF₃ formation from CF₃CHO photolysis. We employed the Tropospheric Ultraviolet and Visible (TUV) radiation model (version 5.4) at two representative latitudes—equatorial and 40°N—in order to capture solar fluxes characteristic of tropical and mid-latitude regions during the spring equinox. By combining the simulated photon fluxes with our parameterization of $\Phi(\text{total})$ and $\Phi(\text{CHF}_3)$ as well as the absorption cross section, we derived altitude-dependent photolysis rates (J values) for CF₃CHO and for CHF₃ formed from R1b channel, respectively. To account for the pressure dependence of $\Phi(\text{total})$ and $\Phi(\text{CHF}_3)$ with altitude, we applied the existing Stern–Volmer analyses reported by (Van Hooymissen et al., 2025) to our parameterized quantum yields obtained at atmospheric pressure (see Figure A2-5). This approach allows a more realistic representation of the altitude-dependent photolysis behaviour of CF₃CHO and the associated production of CHF₃. Accordingly, the photolysis rate coefficient, J , is defined as:

$$J = \int \sigma(\lambda) \phi(\lambda) F(\lambda) d\lambda \quad \text{Equation 2 – 5}$$

here, $\sigma(\lambda)$ denotes the wavelength-dependent absorption cross section of CF_3CHO , $\Phi(\lambda)$ denotes the $\Phi(\text{total})$ and $\Phi(\text{CHF}_3)$ accounted for pressure- and wavelength- dependence, and $F(\lambda)$ denotes the photon flux simulated from the TUV model at either equator or 40°N .

Additionally, reaction with OH is widely recognized as another dominant atmospheric sink for CF_3CHO . Recent theoretical work by (Long et al., 2022) highlighted that HO_2 may also play a significant role in CF_3CHO removal. We therefore also considered the oxidation loss of CF_3CHO through reactions with OH and HO_2 . For the reaction of $\text{OH} + \text{CF}_3\text{CHO}$, the temperature-dependent bimolecular rate coefficient (k) (McGillen et al., 2020a) together with representative atmospheric [OH] profile (Brasseur and Solomon, 2005) was used to calculate the first-order loss rate:

$$\text{OH loss rate} = k \cdot [\text{OH}] \quad \text{Equation 2 – 6}$$

For the reaction of $\text{HO}_2 + \text{CF}_3\text{CHO}$, we took the forward and reverse rate coefficients recommended by (Long et al., 2022) and assumed that reaction with NO is the dominant sink for the RO_2 radicals formed in this reaction.

$$\text{HO}_2 \text{ loss rate} = K \cdot [\text{HO}_2] \cdot k_{\text{RO}_2+\text{NO}} \cdot [\text{NO}] \quad \text{Equation 2 – 7}$$

here, K denotes the theoretical equilibrium constant for the $\text{HO}_2 + \text{CF}_3\text{CHO}$ reaction, $[\text{HO}_2]$ and $[\text{NO}]$ denote typical atmospheric concentration profiles of HO_2 and NO respectively (Brasseur and Solomon, 2005), and $k_{\text{RO}_2+\text{NO}}$ is the assumed rate coefficient from analogous RO_2 reactions with NO (Atkinson et al., 2004).

From the above considerations, the atmospheric lifetime of CF_3CHO with respect to these loss processes is shown in Figure 2-14 (a). It is evident that once the pressure dependence of photolysis is included, photolysis dominates as the primary sink throughout the troposphere and stratosphere. A combined gas-phase lifetime was derived by summing all removal pathways, with oxidation making only below ~ 15 km. The lifetime of CF_3CHO , as expected, decreases markedly with altitude, as stronger photon flux drives faster photolysis, leading to the loss rate in the upper stratosphere nearly two orders of magnitude faster than those at the surface.

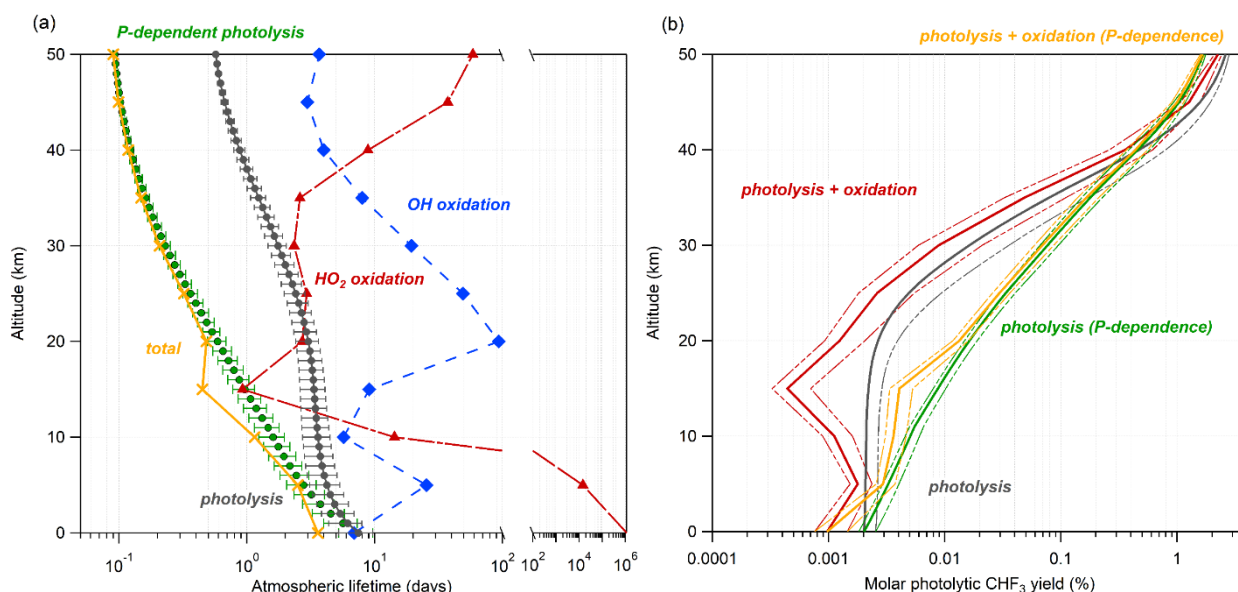


Figure 2-14. *Panel (a):* estimated atmospheric lifetimes of CF_3CHO from 0-50 km, considering individual loss processes via photolysis (grey), OH (blue) and HO_2 (red) oxidation. A pressure-dependent photolysis pathway (green), extrapolated from (Van Hoomissen et al., 2025) (see main text for details), is also shown and combined with oxidation pathways to yield total lifetime. Altitude-resolved radiation fluxes are based on the TUV model at the Equator and 40 °N (displayed by error bars). *Panel (b):* Molar yield of CHF_3 as a function of altitude under different scenarios: photolysis, combined photolysis and oxidation, pressure-dependent photolysis, pressure-dependent combined photolysis and oxidation. Pressure dependence of CHF_3 yield was extrapolated from (Van Hoomissen et al., 2025) (see main text for details).

The competition among these atmospheric sinks was accounted for in order to quantify the altitude-dependent molar yield of CHF_3 from CF_3CHO , as shown in Figure 2-14 (b). It is clear that oxidation by OH and HO_2 slightly decreases the CHF_3 yield in the lower atmosphere. Overall, the production of CHF_3 is highly sensitive to altitude, spanning nearly four orders of magnitude. This strong dependence arises because photolysis at higher altitudes occurs at shorter wavelengths with larger quantum yields, reflecting both the increase of photon flux and the decrease in pressure. These results highlight that the significance of CHF_3 formation is closely tied to the altitude at which CF_3CHO is released, and in other words, the contribution of CF_3CHO photolysis to CHF_3 production depends strongly on the location of its precursor emissions in the atmosphere and the capability of these fluorinated precursors to migrate to the upper atmosphere. For instance, if a long-lived fluorinated precursor is

transported into the stratosphere, its indirect GWP will increase accordingly. In this sense, this concept is analogous to the “fractional release factors” encountered in ODP calculations.

To further investigate this, we assessed the atmospheric transport potentials of representative F-gases containing CF_3CH_2- or $\text{CF}_3\text{CH=}$ moieties, including HFOs, HFEs, HCFCs, halons, and HFCs, and summarized the results in Figure 2-15. To link the atmospheric lifetimes of these species with large-scale vertical transport, we used OH rate coefficients determined either from laboratory measurements (McGillen et al., 2020a) or structure–activity relationships (Kwok and Atkinson, 1995; McGillen et al., 2024; Michelat et al., 2022), which represent their dominant sink. The indicative ellipses in Figure 2-15 therefore reflect the range of reactivity (maximum and minimum OH rate constants) and are superimposed on average age of air, providing an approximate measure of vertical transport timescales. According to this analysis, degradation of HFOs is essentially confined to the troposphere, suggesting that their indirect GWP from CF_3CHO photolysis is negligible. In contrast, many long-lived HFCs, HCFCs, halons, and HFEs are of greater concern, since they persist long enough to reach the stratosphere, where molar yields of CHF_3 can increase sharply.

However, we considered that a variety of factors can influence the eventual formation of CF_3CHO from such long-lived species, including transport dynamics, variability in OH and $\text{O}(^1\text{D})$ fields, and the efficiency of troposphere–stratosphere exchange. These complex interactions are best captured by an atmospheric model.

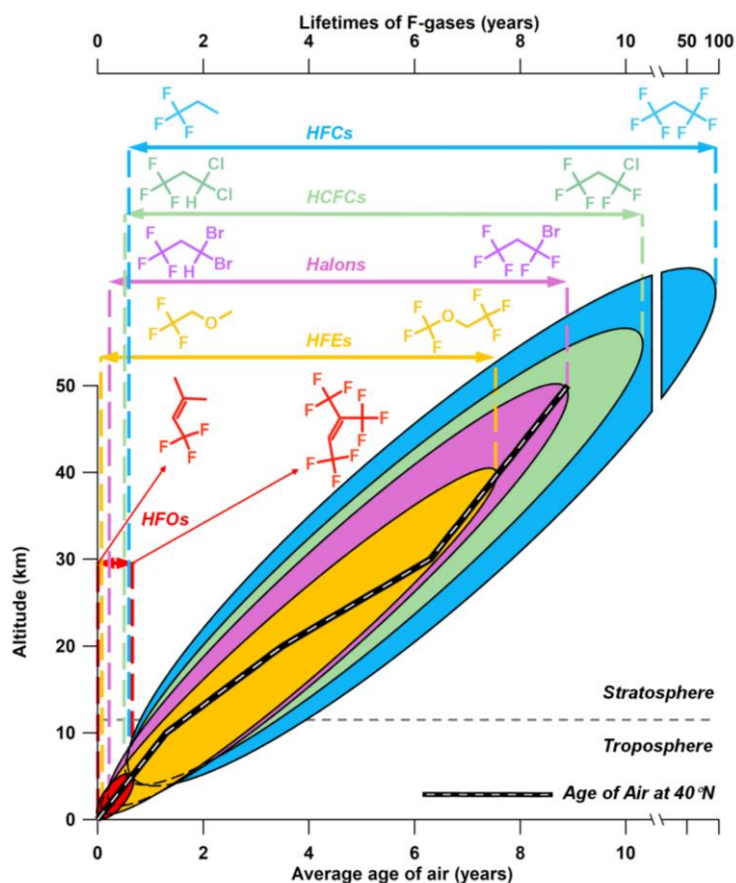


Figure 2-15. Distribution of representative fluorinated species in the atmosphere based on OH reactivity and estimated lifetimes, overlaid with average age of air as a function of altitude. Each coloured region corresponds to a compound class (HFOs, HFEs, HCFCs, halons, HFCs), with carbon number restrictions ($C < 5$ for HFOs; $C < 3$ for HFEs, HCFCs, halons, and HFCs). Representative structures for the longest- and shortest-lived molecules in each class are shown. The black line indicates the mean age of air at 40°N .

In the case study presented in Figure 2-16, we selected the long-lived HFC-143a as a representative precursor species (atmospheric lifetime of ~ 51 years) and extracted an existing two-dimensional model output to characterize its losses in the atmosphere (Newman et al., 2013). The model indicates that even for such a persistent compound, roughly 90% loss occurs in the troposphere, while only $\sim 10\%$ is lost in the upper atmosphere through reactions with OH and $\text{O}(^1\text{D})$. We then mapped this loss profile of HFC-143a onto the effective yields of CHF_3 via CF_3CHO (see Figure 2-16). By integrating the CHF_3 effective yield profile within 0–50 km, we derive a total of 0.03% CHF_3 yield from HFC-143a depletion. If only direct GWP is considered, HFC-143a has a 100-year GWP of 5900, typically viewed as much

lower than that of HFC-23 (14,700). When the secondary production of HFC-23 through CF_3CHO photolysis is included, the effective GWP of HFC-143a increases marginally to 5904. Therefore, this calculation demonstrates that even though the yield of CHF_3 increases significantly at altitude, this is not enough to affect the GWP of even a long-lived F-gas. Therefore, even in extreme cases such as HFC-143a, we can anticipate, with the best information currently available that this photolytic source of CHF_3 is insufficient to explain the discrepancies between top-down and bottom-up estimates of CHF_3 in the atmosphere. This would indicate that other phenomena are responsible for such disagreements, which may indicate that other secondary sources (e.g., ozonolysis (McGillen et al., 2023)) or fugitive emissions may warrant further attention.

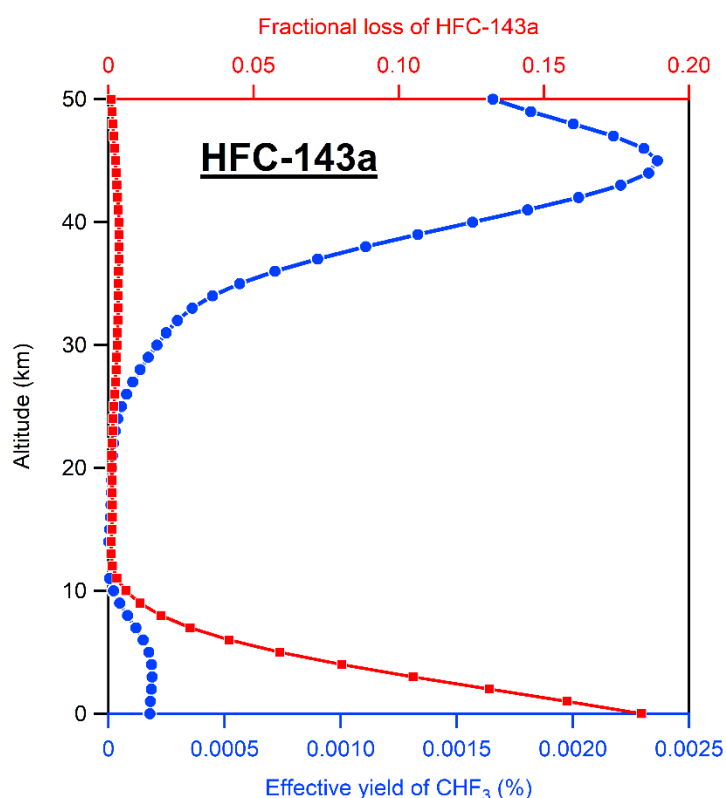


Figure 2-16. Altitude-resolved fractional loss of a representative long-lived F-gas, HFC-143a, and correspondingly effective CHF_3 molar yield. Red line and top axis show the fractional atmospheric loss of HFC-143a, based on a 2-D chemical transport model (SPARC, 2013). Blue line and axis (bottom) show the effective molar yield of CHF_3 , obtained by mapping the simulated CF_3CHO formation field (normalized to a yield of unity from HFC-143a degradation) onto the altitude-dependent CHF_3 yields from the photolysis of CF_3CHO (see Figure 2-14, panel b).

2.5 Conclusions

In this chapter, we investigated the photochemical reaction of CF_3CHO at 248 nm and throughout actinic range via a series of single-wavelength and broadband UV experiments, enabling the determination of absolute photolysis quantum yields for CF_3CHO and for the branching channel to make HFC-23 (one of the most potent greenhouse gases). Correspondingly, this allows us to parameterize their wavelength dependence in the 280-320 nm wavelength range. To place these new data in an atmospheric context, we combined our parameterizations with recently reported pressure dependencies, theoretical calculations of the HO_2 reaction, and experimental results on OH reactivity, thereby enabling a more accurate assessment of CHF_3 production. By superimposing the atmospheric lifetimes and vertical transport potentials of fluorinated precursors to CF_3CHO , we were able to characterize the enhancement of indirect GWP from CHF_3 formation through CF_3CHO photolysis. This provides crucial insights for policymakers aiming to better assess the climate implications of secondary atmospheric chemistry and make informed regulatory decisions regarding industrial F-gases.

In the future, as the number of F-gases expands and increasingly complex fluorinated structures are introduced, continuous monitoring of their degradation pathways and by-products will be essential. Our results emphasize the importance of accurately characterizing atmospheric lifetimes and degradation products to ensure that the next generation of refrigerants and industrial solvents indeed deliver on their intended climate and environmental benefits.

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Appendices: Chapter 2

Table A2-1. Summary of experimental conditions and the obtained CF₃CHO quantum yields in 248, 290, 300, 310, 315, 320 nm photolysis of CF₃CHO.

wavelength ^a	Φ_{total}^b	[CF ₃ CHO] ^c	OH scavenger	[scavenger] ^c	actinometer	[actinometer] ^c	bath gas	photolysis time ^d	p ^e	T ^f	detection method
248	0.827±0.053	5.76×10 ¹⁵	CO	2.02×10 ¹⁸	HNO ₃	1.12×10 ¹⁵	zero air	0.11	785	298	FTIR
248	0.833±0.053	4.80×10 ¹⁵	CO	2.20×10 ¹⁸	HNO ₃	6.41×10 ¹⁴	zero air	0.11	779	298	FTIR
290	0.580±0.061	1.02×10 ¹⁶	CO	8.52×10 ¹⁷	CH ₃ I	2.06×10 ¹⁶	zero air	10.87	766	298	FTIR
290	0.591±0.062	8.75×10 ¹⁶	CO	3.09×10 ¹⁸	CH ₃ I	2.99×10 ¹⁶	zero air	8.06	772	298	FTIR
290	0.584±0.062	3.37×10 ¹⁶	CO	2.95×10 ¹⁸	CH ₃ I	1.14×10 ¹⁶	zero air	23.26	772	298	FTIR
300	0.403±0.042	1.16×10 ¹⁶	CO	7.62×10 ¹⁷	CH ₃ I	2.42×10 ¹⁶	zero air	11.46	768	298	FTIR
300	0.384±0.040	3.60×10 ¹⁵	CO	7.76×10 ¹⁷	CH ₃ I	2.11×10 ¹⁶	zero air	9.6	770	298	FTIR
310	0.191±0.024	3.32×10 ¹⁶	CO	1.68×10 ¹⁸	CH ₃ I	1.33×10 ¹⁷	zero air	18.72	768	298	FTIR
310	0.172±0.022	9.63×10 ¹⁵	CO	7.84×10 ¹⁷	CH ₃ I	2.16×10 ¹⁶	zero air	9.63	770	298	FTIR
315	0.101±0.013	3.28×10 ¹⁶	CO	2.33×10 ¹⁸	CH ₃ I	1.92×10 ¹⁷	zero air	24.92	772	298	FTIR
320	0.0731±0.012	2.29×10 ¹⁶	CO	1.67×10 ¹⁸	CH ₃ I	1.92×10 ¹⁷	zero air	20.22	769	298	FTIR

^aUnits of nanometer. ^bDimensionless quantum yield. ^cConcentrations, denoted by [X] are in units of molecule cm⁻³. ^dPhotolysis duration in hours. For 248 nm laser experiments, effective irradiation time is reported instead of laser pulses for better comparison. ^eUnits of Torr. ^fUnits of Kelvin.

Table A2-2. Summary of experimental conditions and the obtained CHF₃ quantum yields and molar yields in 248, 290, 300, 310, 315, 320 nm photolysis of CF₃CHO.

wavelength ^a	$\Phi_{\text{CHF}_3}^b$	$Y_{\text{CHF}_3}^c$	[CF ₃ CHO] ^d	OH scavenger	[scavenger] ^d	bath gas	photolysis time ^e	p ^f	T ^g	CHF ₃ detection method
248	0.286±0.023	0.344±0.028	1.06×10 ¹⁶	CO	1.52×10 ¹⁸	zero air	0.23	783	298	FTIR
248	0.290±0.024	0.350±0.028	1.08×10 ¹⁶	CO	1.16×10 ¹⁸	zero air	0.18	780	298	FTIR
290	(2.80±0.36)×10 ⁻³	(4.78±0.62)×10 ⁻³	1.17×10 ¹⁶	CO	9.65×10 ¹⁷	zero air	9.74	770	298	SPIRIT
290	(2.86±0.37)×10 ⁻³	(4.90±0.63)×10 ⁻³	1.30×10 ¹⁶	CO	2.63×10 ¹⁸	zero air	9.67	769	298	SPIRIT
300	(1.44±0.19)×10 ⁻⁴	(3.66±0.47)×10 ⁻⁴	1.22×10 ¹⁶	CO	9.12×10 ¹⁷	zero air	10.5	768	298	SPIRIT
300	(1.28±0.16)×10 ⁻⁴	(3.25±0.42)×10 ⁻⁴	1.19×10 ¹⁶	CO	1.22×10 ¹⁸	zero air	10.42	767	298	SPIRIT
300	(1.55±0.20)×10 ⁻⁴	(3.94±0.51)×10 ⁻⁴	1.27×10 ¹⁶	CO	2.11×10 ¹⁸	zero air	28.59	771	298	SPIRIT
300	(1.41±0.18)×10 ⁻⁴	(3.59±0.46)×10 ⁻⁴	1.38×10 ¹⁶	CO	2.47×10 ¹⁸	zero air	24.58	770	298	SPIRIT
305	(4.09±0.65)×10 ⁻⁵	(1.36±0.25)×10 ⁻⁴	1.65×10 ¹⁶	CO	2.54×10 ¹⁸	zero air	25.23	769	298	SPIRIT
310	BDL ^h	BDL ^h	1.19×10 ¹⁶	CO	1.54×10 ¹⁸	zero air	9.35	771	298	SPIRIT

^aUnits of nanometer. ^bDimensionless quantum yield. ^cDimensionless molar yield. ^dConcentrations, denoted by [X] are in units of molecule cm⁻³. ^ePhotolysis duration in hours. For 248 nm laser experiments, effective irradiation time is reported instead of laser pulses for better comparison. ^fUnits of Torr. ^gUnits of Kelvin.

Table A2-3. Summary of CF₃CHO photolysis quantum yields and CHF₃ product yield from literature and this work.

248	Xe Arc lamp, 450W, with monochromator	reactor	FTIR	296	760	Zero Air	O ₂ , CO	HNO ₃	0.830±0.053	0.234±0.019	this work
248	KrF Excimer laser	reactor	FTIR and GC/MS	295	650-678	N ₂	NO	CF ₂ BrCF ₂ Br	1.03±0.06	0.358±0.023	(Van Hoomissen et al., 2025)
254	UV-C fluorescent lamps, 55 W, 10 nm	Indoor chamber	FTIR	295±5	10-700	N ₂ or Air	O ₂ , NO	CH ₃ CHO	0.52±0.07	0.16±0.02	(Sulbaek Andersen et al., 2006)
254	low-pressure Hg Arc lamp, 10W	Indoor chamber	FTIR	297	15-56	NO	NO	(CF ₃ CO) ₂ O	0.79±0.09	0.38±0.07	(Chiappero et al., 2006)
266	4th harmonic Nd:YAG	reactor	FTIR and GC/MS	295	650	N ₂	NO	CF ₃ I	0.94±0.09	0.407±0.023	(Van Hoomissen et al., 2025)
281	doubled Nd:YAG pumped dye laser	reactor	FTIR	295	100-650	N ₂	NO	CF ₃ I	0.54±0.06	0.0564±0.0066	(Van Hoomissen et al., 2025)
290	Xe Arc lamp, 450W, with monochromator	reactor	SPIRIT	296	760	Zero Air	O ₂ , CO	CH ₃ I	0.587±0.062	(2.83±0.36)×10 ⁻³	this work
300	Xe Arc lamp, 450W, with monochromator	reactor	SPIRIT	296	760	Zero Air	O ₂ , CO	CH ₃ I	0.393±0.041	(1.42±0.18) ×10 ⁻⁴	this work
305	Xe Arc lamp, 450W, with monochromator	reactor	SPIRIT	296	760	Zero Air	O ₂ , CO	CH ₃ I	0.204±0.028	(4.09±0.65) ×10 ⁻⁵	this work
308	XeCl Excimer laser	reactor	GC/MS	295	100-650	N ₂	NO	CF ₃ I	0.830±0.053	(3.02±1.19) ×10 ⁻⁴	(Van Hoomissen et al., 2025)
308	XeCl Excimer laser	reactor	CP-FTMW	5 or 295	0-760	N ₂	NO	HNO ₃	0.19±0.05	(2.3±0.4) ×10 ⁻⁴	(Thomson et al., 2025)
308	XeCl Excimer laser	Indoor chamber	FTIR	295	100-700	N ₂	NO	CH ₃ CHO	0.17±0.03	<0.02	(Chiappero et al., 2006)

Continued from Table A2-3 on the previous page

310	Xe Arc lamp, 450W, with	reactor	SPIRIT	296	760	Zero Air	O ₂ , CO	CH ₃ I	0.181±0.023		this work
313	Hg Arc lamp, 250 W, K ₂ CrO ₄ filter	Indoor chamber	FTIR and MS	291-673	0.5-100	CF ₃ CHO		(CH ₃) ₂ CO	0.12		(Dodd and Smith, 1957)
313	Hg Arc lamp, 100 W, 10 nm FWHM	Indoor chamber	FTIR	303-423	8.6-146.7	N ₂	O ₂				(Pearce and Whytock, 1971)
315	Xe Arc lamp, 450W, with	reactor	SPIRIT	296	760	Zero Air	O ₂ , CO	CH ₃ I	0.101±0.013		this work
320	Xe Arc lamp, 450W, with	reactor	SPIRIT	296	760	Zero Air	O ₂ , CO	CH ₃ I	0.0731±0.012 ⁷		this work
366	Hg Arc lamp, 100 W	Indoor chamber	FTIR		712	N ₂	O ₂				(Richter et al, 1992)
broad band	nature sunlight	outdoor chamber	FTIR	298±2	760	Zero Air	O ₂ , NO		<0.02		(Sellevåg et al., 2004)
broad band	UV-B lamps (290-400 nm)	Indoor chamber	FTIR	298±2	760	Zero Air	O ₂ , NO		See Figure 2-1	<0.003	(Sulbaek Andersen and Nielsen, 2022)

^aUnits of nanometers. ^bFTIR: Fourier transform infrared spectroscopy; GC/MS: gas chromatography/mass spectrometry; SPIRIT: SPectromètre Infra-Rouge In situ Toute altitude; CP-FTMW: chirped-pulse, Fourier-transform microwave spectrometry. ^cUnits of Kelvin. ^dUnits of Torr. ^eReported quantum yields at room temperature and the maximum pressure of the specified pressure range.

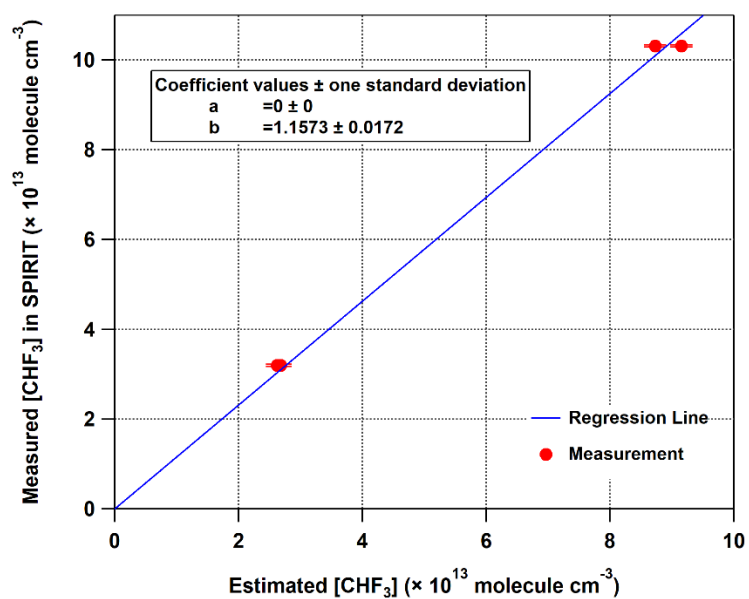


Figure A2-1. Calibration of SPIRIT detection of CHF₃ using known concentrations of standard CHF₃ gas. This calibration was used to validate SPIRIT's quantitative response and ensure accurate CHF₃ quantification in photolysis experiments.

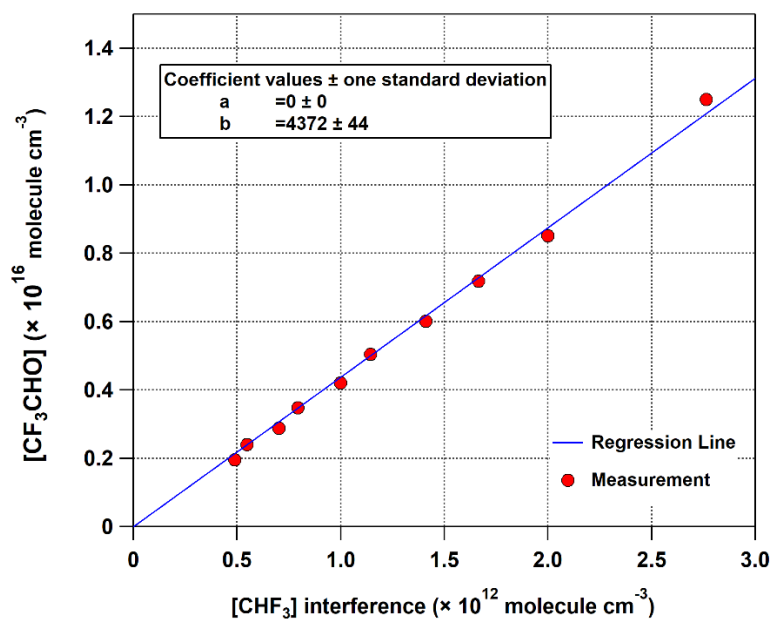


Figure A2-2. Linear relationship between CF₃CHO concentration and CHF₃ interference signal detected by SPIRIT. The observed signal arises from spectra overlap between CF₃CHO and CHF₃ in the infrared region. This calibration was used to correct CHF₃ quantification in the experiments.

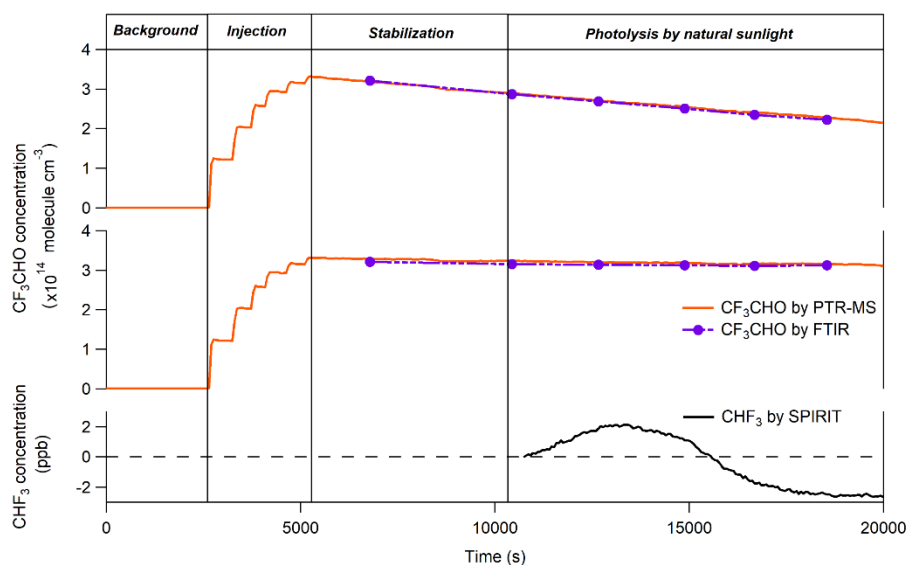


Figure A2-3. Upper panel: time-series of CF_3CHO photolytic loss by natural sunlight in HELIOS chamber, monitored simultaneously by PTR-ToF-MS (orange line) and FTIR (purple line). Middle panel: PTR-ToF-MS data were corrected for instrumental stability, wall loss, and dilution based on the *stabilization* phase. FTIR data were corrected for dilution traced by SF_6 measurement. Lower panel: corrected CHF_3 concentration (black line) detected *in situ* by SPIRIT in the *photolysis* phase.

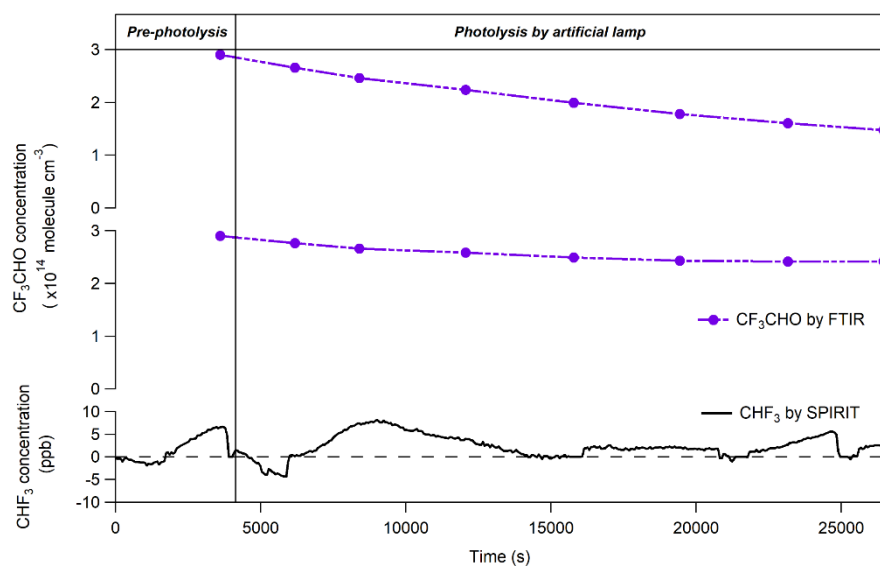


Figure A2-4. Upper panel: time-series of CF_3CHO photolytic loss by artificial light in HELIOS chamber, monitored by FTIR (purple line). Middle panel: FTIR data were corrected for dilution traced by SF_6 measurement. Lower panel: corrected CHF_3 concentration (black line) detected *in situ* by SPIRIT in the *photolysis* phase.

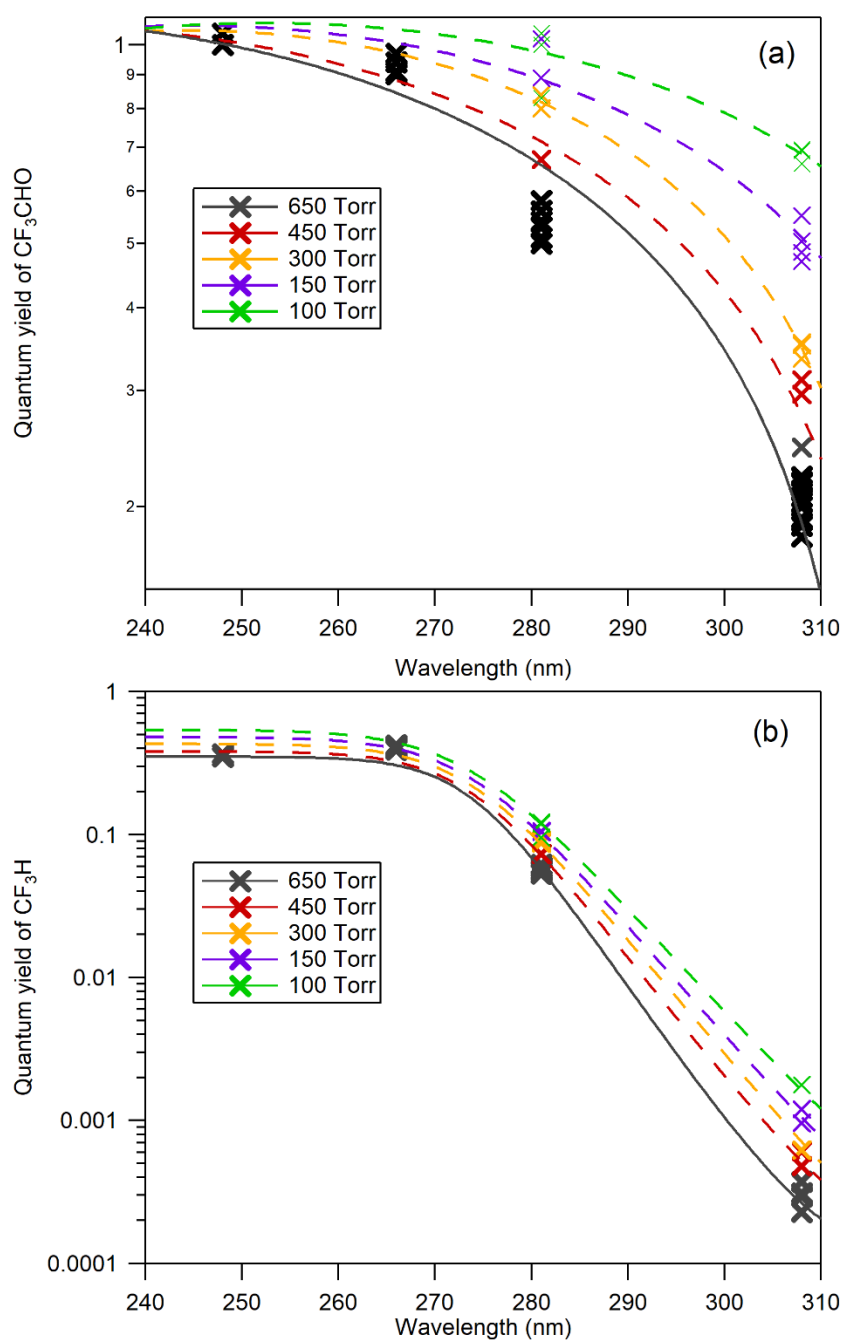


Figure A2-5. Wavelength-dependent quantum yields of (*panel (a)*) CF_3CHO loss and (*panel (b)*) CHF_3 formation at different total pressures (100–650 Torr), based on data fitted and extrapolated from (Van Hoomissen et al., 2025). Symbols indicate experimental values, and fitting lines represent pressure-dependent extrapolated trends.

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Chapter 3:

**Developing a relative rate technique for measuring
Criegee intermediate reactivity**

3.1 Introduction

Alkene ozonolysis has long been recognized as a significant source of atmospheric oxidants and of compounds that act as precursors to secondary organic aerosol (SOA). This is relevant to the formation of highly reactive Criegee intermediates (CIs), which could then engage in a range of complex chemical processes (Donahue et al., 2011). A quantitative understanding of the relative importance of these downstream pathways requires reliable kinetic data. However, despite the importance of this chemistry, there is still a lot that remains unknown about the kinetics of these reactions. This is partly because of the limitations of current absolute kinetic methods, which rely on *gem*-diiodo- (Welz et al., 2012) and dihaloalkane (Peltola et al., 2024) CI precursors. In this chapter, we will introduce a chamber-based relative rate technique that employs highly symmetrical alkenes (such as ethene) as precursors, offering a convenient route to expand the kinetic database of CI reactions and new opportunities to explore previously inaccessible reaction systems.

Upon reaction with ozone (O_3), alkenes are ozonized via 1,3-cycloaddition, producing a varied array of carbonyl oxides, commonly known as Criegee intermediates (CI). A significant portion of these intermediates is produced in a thermally excited state, possessing excess internal energy that facilitates a rapid unimolecular reaction, yielding a number of radical and stable products (McGillen et al., 2023; Vereecken and Francisco, 2012; Welz et al., 2012). The remaining fraction is either formed in a “cold” state or becomes collisionally stabilized through interactions with inert atmospheric molecules, giving rise to stabilized Criegee intermediates (SCIs). Unlike their excited counterparts, SCIs can persist long enough to engage in a wide range of bimolecular reactions. For instance, these SCIs can insert into labile hydrogenous bonds, such as those present in organic acids, alcohols, amines, sulfides and even water. Among these, reactions with $(H_2O)_2$ (Lade et al., 2024), and in more polluted environments, with SO_2 are considered to be effective atmospheric sinks for SCIs (Boy et al., 2013). However, recent field measurements of the insertion products of formaldehyde oxide into relatively unreactive hydroperoxides suggest that reactions with water vapor may be less dominant than previously assumed (Caravan et al., 2024).

To better constrain the atmospheric impacts of SCIs, a detailed understanding of their bimolecular reactivity is essential (Vereecken et al., 2018). However, the chemical space relevant to SCI reactions is both vast and sparsely explored as shown in Figure 3-1 (Ervens et al., 2024).

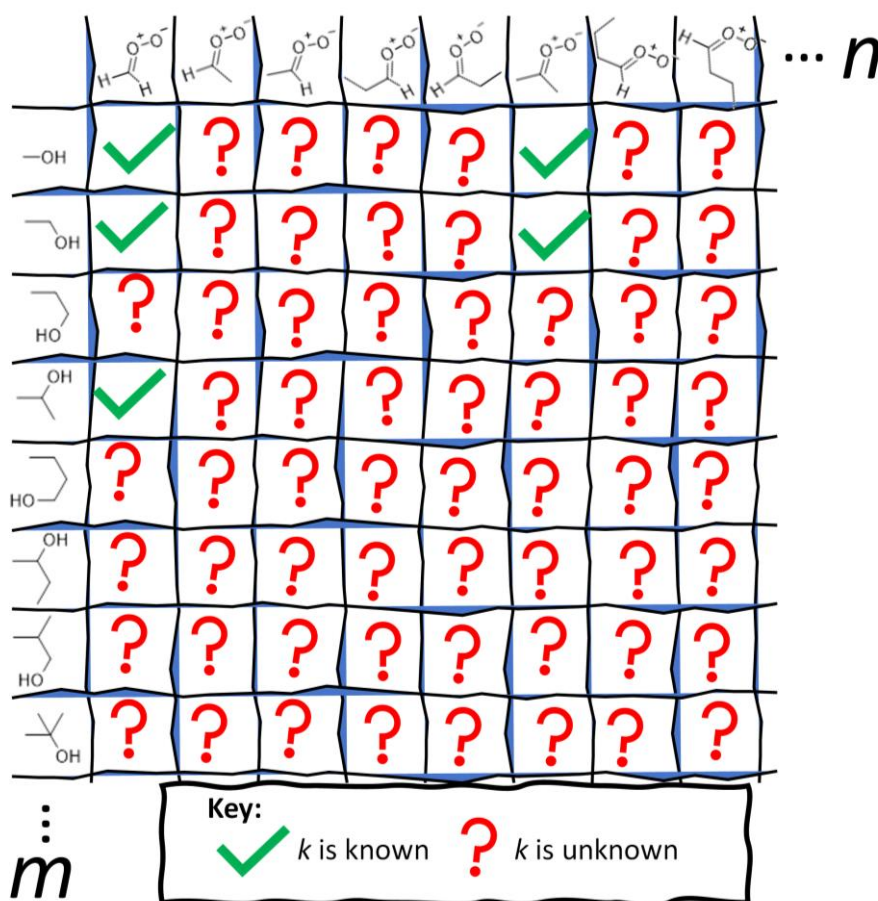


Figure 3-1. An example of the parameter space of the reactions of stabilized Criegee intermediate reactions visualized as a sparsely populated $m \times n$ matrix in which m and n denote the number of possible co-reactants and SCIs respectively. The exact sizes of m and n are unknown, but are assumed to be extremely large.

The first dimension of this complexity arises from the large number of alkenes emitted into the atmosphere (Carter, 2015), from both biogenic and anthropogenic sources, each capable of yielding multiple CIs with distinct structures and reactivities (McGillen et al., 2017; Vereecken et al., 2017). Consequently, the total number of structurally unique SCIs (denoted as n herein) that may form under atmospheric conditions is substantial. The second dimension involves the wide range of atmospheric compounds that SCIs can potentially react with. These include molecules possessing labile hydrogen

atoms, such as carboxylic acids, alcohols, amines, sulfides, and hydroperoxides, as well as other unsaturated or electrophilic compounds with reactive double bonds or carbonyl functionalities (Wang et al., 2025). Each of these represents a distinct class of co-reactants (denoted as m herein), many of which vary widely in volatility, concentration, and functional group chemistry. This combinatorial expansion defines a reaction landscape that can be conceptualized as an $m \times n$ matrix, where each element represents a unique bimolecular reaction between a specific SCI and a specific atmospheric co-reactant. As shown in Figure 3-1, only a limited subset of this space has been experimentally characterized, leaving the majority of potential reactions unexplored. The sparse coverage not only reflects the experimental difficulties in generating and isolating individual SCIs, but also highlights the need for efficient, generalizable kinetic measurement techniques that can systematically expand our understanding of SCI reactivity across this chemically rich domain.

Over the past decade, substantial progress has been made in elucidating both unimolecular and bimolecular reaction pathways of CIs, largely enabled by the advent of synthetic *gem*-diiodoalkane precursors and refined detection methods such as cavity ring-down spectroscopy (CRDS, as shown in Figure 3-2) and photoionization mass spectrometry (Beames et al., 2012; Su et al., 2013; Welz et al., 2012). These advances have allowed for the controlled generation of specific SCI structures and provided access to absolute kinetic measurements under pseudo-first-order conditions.

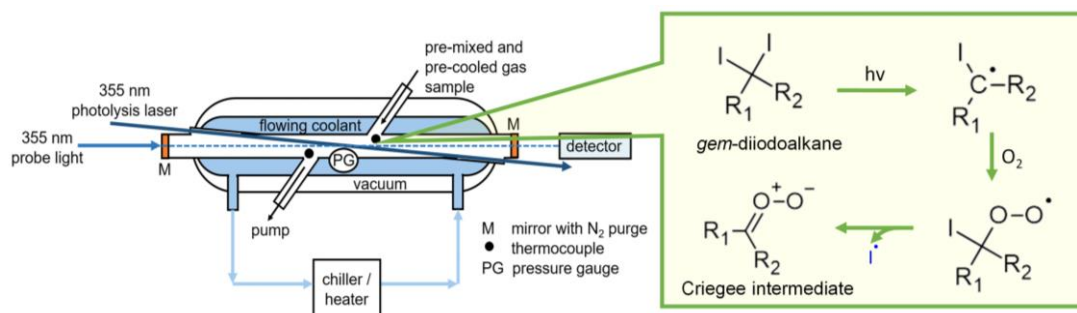


Figure 3-2. Schematic of cavity ring-down instrumentation (CRDS) alongside the formation of Criegee intermediate via photolysis of *gem*-diiodoalkane precursor.

Nevertheless, despite these methodological breakthroughs, several intrinsic limitations remain. These are summarized as follows:

- **Limited precursor availability:** With the exception of diiodomethane, most gem-diiodoalkanes are not commercially available and must be synthesized on demand. This adds logistical and financial burdens that can slow down kinetic measurements and limit molecular diversity.
- **Low volatility of precursors:** The presence of two heavy iodine atoms significantly reduces the vapor pressure of these precursors, restricting their use in flow-tube or low-pressure reactor systems and making them unsuitable for reactions involving semi-volatile or low-volatility co-reactants.
- **Excess reactant requirement:** Because most absolute methods operate under pseudo-first-order conditions, the co-reactant must be introduced in large excess to ensure measurable first-order decay. This poses significant challenges for studying reactions involving low volatility or thermally unstable species, for which just a few rate constants have been reported to date (Caravan et al., 2024; Cornwell et al., 2024).
- **Potential systematic biases:** As with any single-technique approach, the possibility of systematic error cannot be excluded. Confounding factors include self-reaction of the SCI, secondary reactions with iodine atoms or photolysis by-products, and spectral interference from overlapping UV absorptions.

Despite these limitations, the consistency of kinetic data obtained across independent studies and different research groups supports the reliability of this technique as a foundational method for deriving SCI kinetics. Accordingly, we aim to expand the methodological toolbox by developing a relative rate technique using a chamber facility that avoids the abovementioned obstacles and can accommodate a broader range of co-reactants in the continued exploration of atmospheric Cl chemistry (see a descriptive diagram in Figure 3-3).

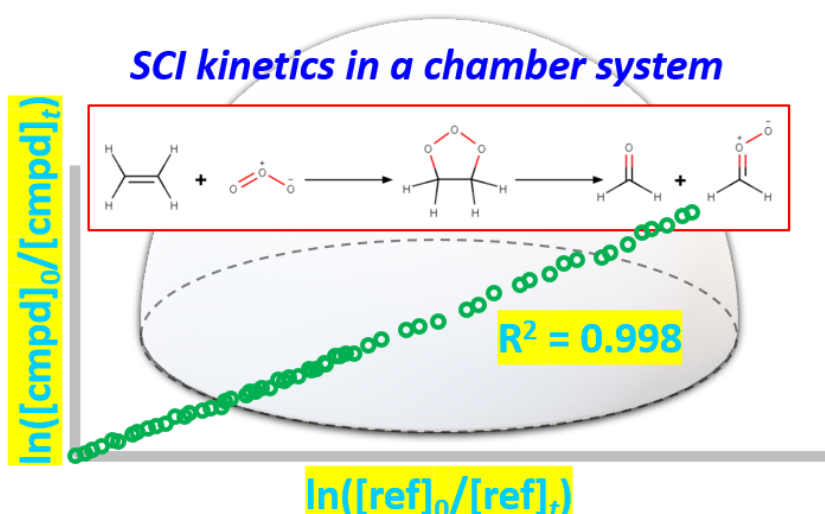


Figure 3-3. Schematic overview of the relative rate technique developed to measure the bimolecular reactivity of stabilized Criegee intermediates (SCIs) in a chamber system.

3.2 Experimental techniques

3.2.1 Chamber experiments

All experiments were performed in the ACTRIS exploratory platform, HELIOS chamber. This facility has been described elsewhere (Ren et al., 2017), and only those features that are pertinent to the current study will be outlined in this chapter 3. This chamber consists of a 90 m³ hemispherical enclosure constructed from UV-transparent FEP Teflon film. This chamber is housed outdoors at CNRS-ICARE (Orléans, France), allowing natural sunlight experiments, yet for the present study, only dark ozonolysis experiments were performed.

Continuous mixing is achieved using two axial fans (20 Hz), which could ensure complete homogenization of chamber contents within approximately two minutes. To prevent contamination from ambient air, the chamber is maintained under a slight overpressure through a continuous flow of purified dry air (50 standard litres per minute). This flow induces gradual dilution of chamber species, which is quantitatively tracked using a unreactive tracer, sulfur hexafluoride (SF_6). By injecting a known initial concentration ($\sim 1.75 \times 10^{12}$ molecule cm⁻³), the time-resolved SF_6 decay is monitored by a

multipass open-path Fourier-transform infrared spectrometer (FTIR, Bruker Vertex 70), with absorption measurements centred around 950 cm^{-1} and a total optical pathlength of 302.06 m.

O_3 is generated using a silent discharge generator (BMT 803 BT), with output concentrations measured either via an in-line UV photometric ozone monitor (BMT 965 ST or Thermo Fisher 49i) or the FTIR. Precise and reproducible reagent injection is achieved using a gas manifold, through which gases such as ozone, ethene, SF_6 , cyclohexane, acids and alcohols are directed into the chamber via a calibrated injection system.

Gas-phase products and reactant are monitored in real time using a Proton Transfer Reaction-Time-of-Flight-Mass Spectrometer (PTR-ToF-MS, IONICON PTR-8000) operated in NH_4^+ mode with an Extended Volatility Range (EVR) drift tube. PTR-MS works through the generation of reagent ions (selectively chosen) in a flow tube, which ionize compounds through proton transfer reactions. The resulting ions are subsequently detected and quantified by a mass spectrometer according to their mass-to-charge ratios (Hansel et al., 1995). In the conventionally used H_3O^+ ion mode, a compound (A) with proton affinity (PA) higher than that of water ($> 697\text{ kJ mol}^{-1}$) can be efficiently ionized (reaction R3-1), and therefore detected by PTR-MS (Hansel et al., 1995; Lindinger et al., 1998).



This technique is particularly well suited for the present study. First, PTR-MS enables continuous, real-time detection of stable gas-phase reactants and products at low amount fractions with high sensitivity and time resolution. In our chamber experiments involving Criegee chemistry, Criegee intermediates are highly short-lived ($\leq 2\text{ ms}$ for CH_2OO) (Welz et al., 2012) and cannot be detected directly by PTR-MS. Therefore, kinetic information must be derived by tracking the time evolution of stable co-reactants and reaction products. Second, the NH_4^+ ionization mode employed in this work provides a softer and more selective ionization option compared to conventional H_3O^+ -based PTR-MS. Because of the higher proton affinity of ammonia ($\text{PA} = 854\text{ kJ mol}^{-1}$), NH_4^+ ionization proceeds predominantly via adduct formation (reaction R3-2), thereby preserving molecular integrity and suppressing extensive fragmentation (Lindinger et al., 1998).



This selectivity is particularly advantageous for the detection of certain oxygenated organic compounds like carbonyls, hydroperoxides, and some other multifunctional molecules, for which extensive fragmentation would otherwise complicate identification (Canaval et al., 2019). Collectively, PTR-MS ensures reliable tracking of individual organics over extended experiments timescales.

A high-throughput sampling system, composed of 1/2" PFA tubing connected to a diaphragm pump (15 SLM flow rate), ensures minimal wall loss and fast response. To reduce sampling artefacts for low-volatility and peroxidic compounds, the sampling line is shortened and subsampled via a short segment of PEEK tubing (~30 cm), enabling residence times below 1 second. The full schematic of techniques for SCI kinetic measurements is shown in Figure 3-4.

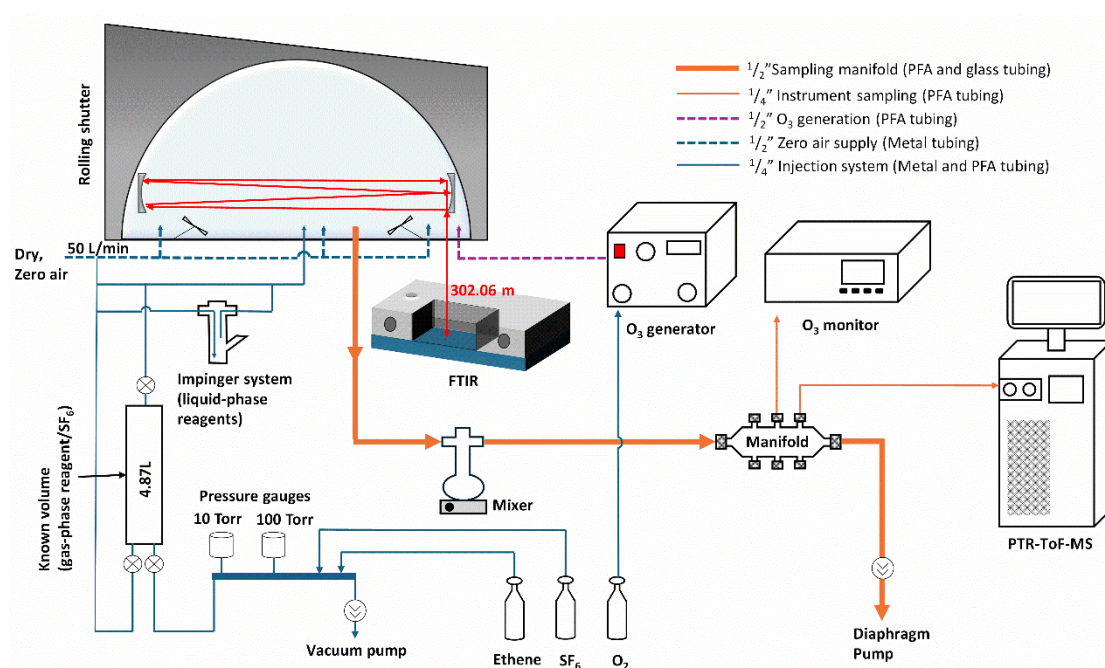


Figure 3-4. Schematic of the experimental setup for measuring SCI kinetics in the HELIOS facility.

3.2.2 Criegee intermediate generation

To ensure well-defined and interpretable oxidation conditions, this study employed two highly symmetrical alkene (ethene for the proof-of-principle study and tetramethylethylene for the extended

measurements), as the precursors for SCI generation. For example, ethene, the simplest alkene of the D_{2h} point group, exhibits perfect molecular symmetry by which it produces a single CI upon ozonolysis, formaldehyde oxide (CH_2OO), without generating structural and conformational isomers (Figure 3-5). This strategy avoids the kinetic complexity that arises when multiple SCIs or isomeric forms are produced concurrently, as commonly observed in the ozonolysis of more complex or asymmetrical alkenes. It thus minimizes the overlap of oxidation pathways and ensures that the system is governed by one well-defined oxidant. Likewise, the same approach is equally applicable to tetramethylethylene (TME) which also undergoes ozonolysis to generate acetone oxide, $(\text{CH}_3)_2\text{COO}$ as the single CI.

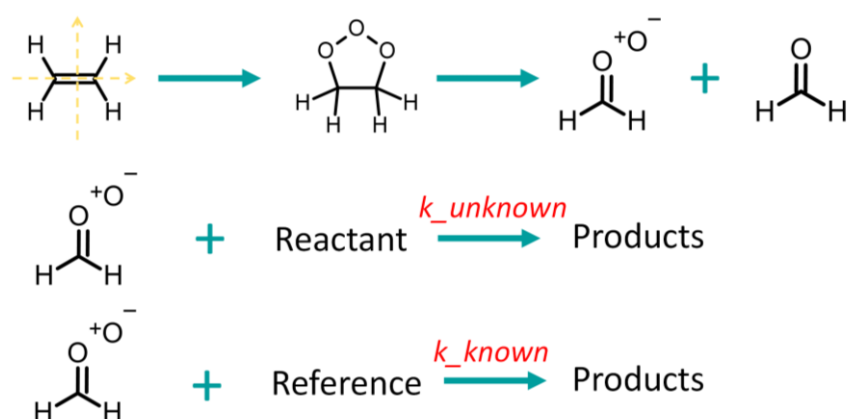


Figure 3-5. Reaction scheme showing the generation of a single type of Criegee intermediate from ethene ozonolysis in a chamber, followed by its concurrent reactions with a target compound and a reference species for relative rate determination.

The choice of CH_2OO for the validation of the method offers several further advantages. First, it is the most extensively studied CI in the literature, especially in absolute kinetic studies, where numerous well-characterized reference rate coefficients are available (McGillen et al., 2017; Welz et al., 2014). This makes it particularly suitable for the present proof-of-principle application of a relative rate technique. Second, CH_2OO is atmospherically relevant because it is formed not only from ethene but also as a major product in the ozonolysis of complex biogenic alkenes such as isoprene (Anglada et al., 2011).

Each experiment was organized into four well-defined phases: *background*, *injection*, *stabilization* and *reactivity*:

First, in the *background phase*, the HELIOS chamber was flushed with zero air for an extended period, typically overnight, to minimize residual gases and surface-absorbed contaminants. Periodic physical or photochemical cleaning was also applied as necessary. This procedure ensured a baseline environment with negligible background signal, as verified by PTR-MS scans across target masses.

Second, the *injection phase* involved the sequential introduction of experimental components: volatile organic co-reactants (e.g., organic acids or alcohols in this study), ozone, and cyclohexane. Here, a large excess of cyclohexane as an OH scavenger was employed to suppress side reactions initiated by OH radicals formed during the unimolecular reactions of CH₂OO. Liquid-phase reactants were typically introduced using a heated impinger, followed by flushing with a stream of zero air to transfer the vapor into the chamber. Concentration stability was confirmed by real-time monitoring using PTR-MS until a steady plateau was reached.

Third, this was followed by a *stabilization phase*, during which the system was allowed to equilibrate. No new reactants were added during this period. Instead, signal stability and loss rates were monitored for each compound to quantify any non-chemical decay, such as dilution, wall deposition and instrumental stability. The information collected here was used to independently determine the first-order loss rate constant.

Finally, in the *reactivity phase*, ethene was introduced in a controlled, stepwise manner to initiate ozonolysis. CH₂OO was generated *in situ*, triggering simultaneous consumption of both the target compound and a reference compound. Their decays were monitored in real time via PTR-ToF-MS. Provided that both species were lost solely through reaction with CH₂OO, and that no regeneration or interfering pathways were active, the relative decay slopes were used to determine second-order rate constants for the compound of interest based on the following Equation 3-1:

$$\ln\left(\frac{[\text{compound}]_0}{[\text{compound}]_t}\right) - k_d t = \frac{k_{\text{compound}}}{k_{\text{reference}}} \ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) - k_d t \quad \text{Equation 3 - 1}$$

Here, [compound]₀ and [compound]_t represent the concentrations of the compound of interest at initial time and time t, respectively. The same notation applies to the reference compounds. The term k_d corresponds to the first-order loss rate due to non-reactive processes such as dilution/wall loss for individual compound.

3.2.3 Chemicals

All reagents used in this study were obtained from commercial sources and used without further purification. Ethene (≥99%, Linde), tetramethylethylene (≥96%, TCI), cyclohexane (≥99.5%, Sigma-Aldrich), acetic acid (≥99.7%, Sigma-Aldrich), propionic acid (≥99%, TCI), butyric acid (≥99%, Sigma-Aldrich), isobutyric acid (≥96%, TCI), pentanoic acid (≥98%, TCI), isopentanoic acid (≥96%, TCI), pyruvic acid (≥96%, TCI), 2-oxobutanoic acid (≥98%, Chem Space), 3-methyl-2-oxobutanoic acid (≥95%, Chem Space), hexanoic acid (≥98%, TCI), pivalic acid (≥99%, TCI), 4-methylpentanoic acid (≥97%, TCI), 3-methylpentanoic acid (≥98%, TCI), methanol (≥99.98%, Acros Organics), ethanol (≥99.5%, Merck), isopropanol (≥99.95%, Fluka), and other alcohols or reference compounds were of analytical grade. Sulfur hexafluoride (SF₆, ≥99.9%) was supplied by Air Liquide. Zero air was generated using a custom-built purification system. Ozone was produced using an ozone generator as described in Section 3.2.2.

3.2.4 Error analysis

The total uncertainties associated with the reported rate coefficients were derived from two principal sources: (1) uncertainties (Δv) in the relative decay slope obtained from linear regression ($\pm 2\sigma$), and (2) the reported uncertainties (Δk_{ref}) in the reference rate coefficients from prior absolute kinetic studies (10-15% depending on the data quality). The final uncertainty was determined using standard error propagation rules:

$$\Delta k = k \times \sqrt{\left(\frac{\Delta v}{v}\right)^2 + \left(\frac{\Delta k_{ref}}{k_{ref}}\right)^2} \quad \text{Equation 3 – 2}$$

where Δk is the total uncertainty, while k is the measured rate coefficient. v is the slope from the relative decay, and k_{ref} is the reference rate coefficient in literature.

When multiple independent determinations of the same reaction were available, e.g., from experiments using different reference compounds or repeated trials, the final recommended value was calculated as a weighted average. The weights were defined as the reciprocal squares of the individual uncertainties ($w_i = 1/\sigma_i^2$), and the final average and uncertainty were computed using the standard Taylor method for weighted means as following equations:

$$k_{ave} = \frac{\sum_i w_i k_i}{\sum_i w_i} \quad \text{Equation 3 – 3}$$

$$\sigma_{ave} = \left(\sum_i w_i \right)^{-1/2} \quad \text{Equation 3 – 4}$$

This method ensures that measurements with smaller uncertainties have proportionally greater influence on the final value, while still incorporating the total experimental variability.

3.3 Results and discussion

3.3.1 Application to CH₂OO + organic acids

Criegee intermediates (CIs) possess the chemical potential to regulate the atmospheric budgets of a variety of tropospheric species. Previous experimental evidence has shown that SCIs react extremely rapidly with organic acids, in some cases approaching the collision limit (Chhantyal - Pun et al., 2017). Therefore, in this study, organic acids were selected as co-reactants for evaluating the reliability of the chamber-based relative rate method. In addition, given the inherent complexity of alkene ozonolysis, we created a custom made zero-dimensional chemical box model, implemented using ACUCHEM (Braun et al., 1988). This model simulates the time-resolved concentration profiles of relevant oxidants and reaction products, enabling us to quantify their individual contributions under our specific experimental conditions. The details of our model are provided in Table A3-1. In brief, the model mechanism was custom-built for these experiments using up-to-date kinetic data acquired from the literature, simulating species concentrations without constraint using an established Ordinary Differential Equation (ODE) solver over the duration of the experiment (Braun et al., 1988).

A representative time-series plot of butyric acid (target compound) and acetic acid (reference compound) is shown in Figure 3-6a, with the key experimental phases clearly truncated as described above. During the stabilization phase, both acids were fully mixed and their signals in PTR-MS were monitored, allowing for correction of individual non-reactive losses, such as wall deposition and dilution (e.g., wall loss, dilution or instrumental stability). The slow ozonolysis rate ($k_{298} = 1.55 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) exhibited by ethene requires a large O_3 (>10 ppm) excess to be present in the chamber, allowing sufficient SCI generation for subsequent bimolecular reactions (IUPAC, 2025).

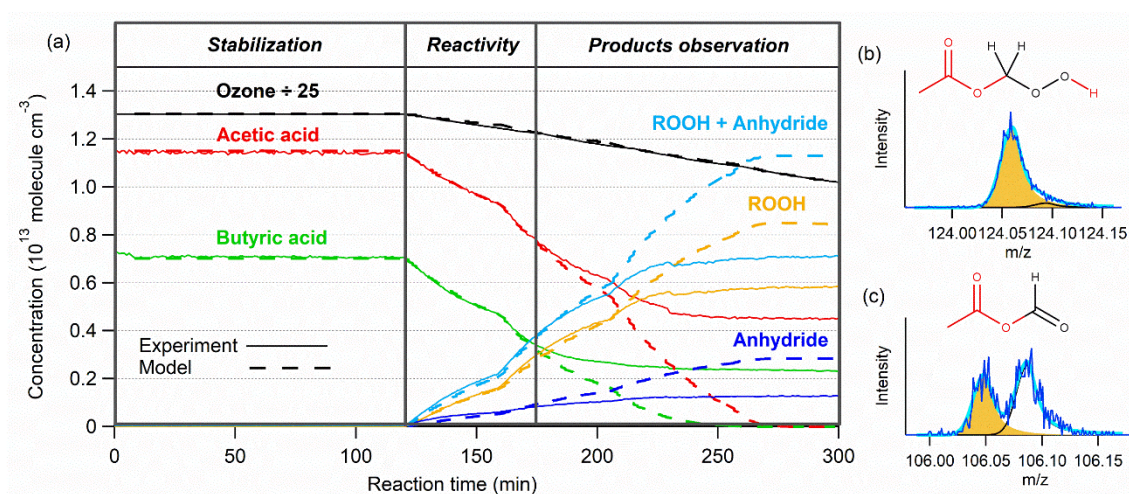


Figure 3-6. Panel (a) Time series of experimental and modelled data of an organic acid relative rate experiment, showing the *stabilization*, *reactivity* and *product observation* phases. Relative rate kinetics are obtained during the *reactivity* phase (see Figure 3-7). Mass spectra of the insertion product into acetic acid (hydroperoxymethyl acetate) and its dehydration product (acetic formic anhydride) are shown in panels (b) and (c) respectively. PTR-MS sensitivities towards these product species are constrained through numerical simulation (see Table A3-1).

Upon initiation of the reactivity phase, following ethene injection, an obvious and simultaneous decline in both ozone and acid concentrations was observed, marking the onset of CH_2OO formation and subsequent bimolecular reactions. The inflection observed at ~160 minutes marked the second ethene injection, further increasing SCI production. Our model assumes instantaneous injections of ethene, which is consistent with the fact that ethene was injected within seconds and mixed within two minutes. The modeled decays of both acids and O_3 indicated excellent agreement with experimental traces up until the period following the second ethene injection.

The high conversion efficiency of acidic reactants was accompanied by the formation of distinct product signals in the PTR-MS (Figures 3-6b and 3-6c), corresponding to α -alkoxyacyl hydroperoxide and their associated dehydrated analogue (anhydride). These product observations support the proposed mechanism in which SCIs react with carboxylic acids via labile hydrogenous bond insertion.

As the chemical complexity of the system increased over time, the model progressively struggled to reproduce the experimental profiles with high fidelity—particularly in the latter stages, where it failed to capture the gradual accumulation and subsequent plateau in product concentrations observed in the PTR-MS data. This arose from the effects of the build-up of products, leading to reaction channels that are as yet not correctly realized in our model. This can also be explained by a second possibility that small interferences on the acetic acid mass accumulate over long time periods. In either case, isolating a well-described reactivity phase for kinetic fitting was necessary to minimize the impact of these effects, whether they are of an analytical or of modelling origin.

The relative decay of butyric acid versus acetic acid was analyzed according to Equation 3-1, as shown in Figure 3-7, demonstrating high linearity and low scatter can be achieved using this method.

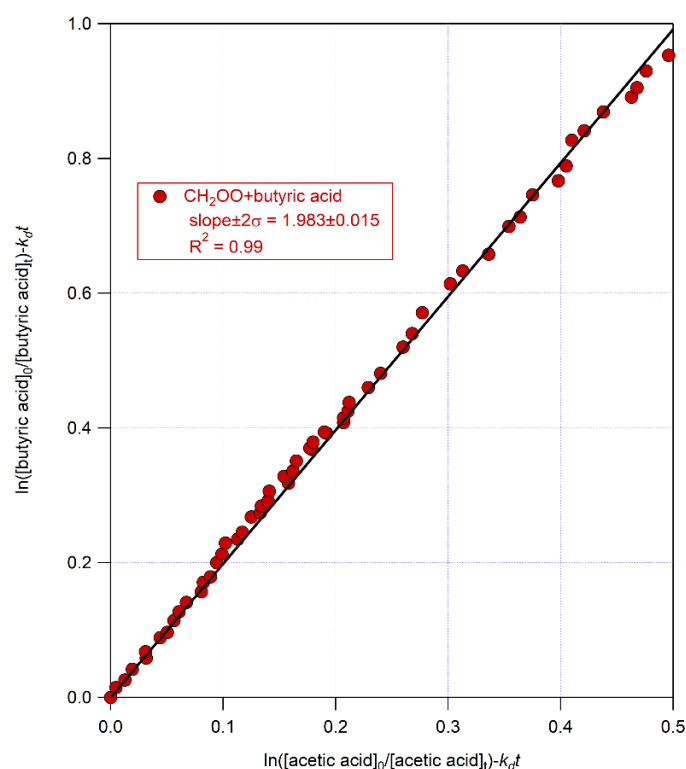


Figure 3-7. Relative rate plot from which kinetics were obtained in the *reactivity phase* of the experiment shown in Figure 3-6a. k_d in the axis label refers to the total first-order loss rate constant (dilution + wall loss + instrumental stability), determined from the *stabilization phase*. Linear regression slope with $\pm 2\sigma$ uncertainty is shown, corresponding to the slope value listed in Table 3-1.

3.3.2 Application to CH₂OO + alcohols

To further test the applicability of the chamber-based relative rate method, we extended our analysis to a series of alcohols, wherein they contain labile O-H bonds susceptible to insertion by SCIs. Compared to carboxylic acids, however, the rate coefficients for alcohol + CH₂OO reactions are considerably lower, typically by three orders of magnitude (McGillen et al., 2017). This renders alcohols a more challenging test case for the developed method and offers a stringent evaluation of the sensitivity of our experimental system.

An equivalent time-series plot for an alcohol experiment is shown in Figure 3-8a, in which the decay of a selection of alcohols was observed in the presence of the reference compound (methanol), upon addition of ethene. O₃ concentration decreased following the ethene injection, marking the formation

of CH₂OO. Due to the low reactivity between CH₂OO and alcohol, higher amounts of O₃ and ethene (leading to increased SCI production) are required for observable conversion compared to acid experiments. As the alcohols were consumed, mass spectral signals corresponding to α -alkoxyalkyl hydroperoxides were observed, along with additional signals attributed to formate esters, formed via dehydration of the parent hydroperoxides.

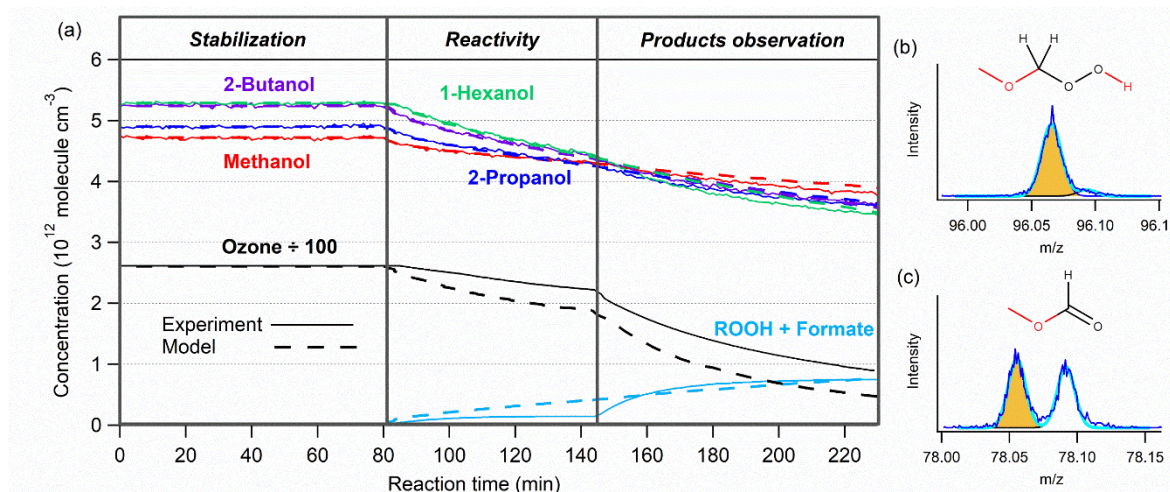


Figure 3-8. Panel (a) Time series of experimental and modelled data of an alcohol relative rate experiment, showing each experimental phase. Kinetics are obtained during the *reactivity phase* (see Figure 3-9). Mass spectra of an insertion product into methanol (hydroperoxymethyl methyl ether) and its dehydration product (methyl formate) are shown in panels (b) and (c) respectively. Sensitivities towards product species are constrained through numerical simulation (see Table A3-1)

By applying Equation 1 to the experimental data, we obtained the relative rate plots shown in Figure 3-9, which again exhibited excellent linearity and minimal scatter across all alcohol systems.

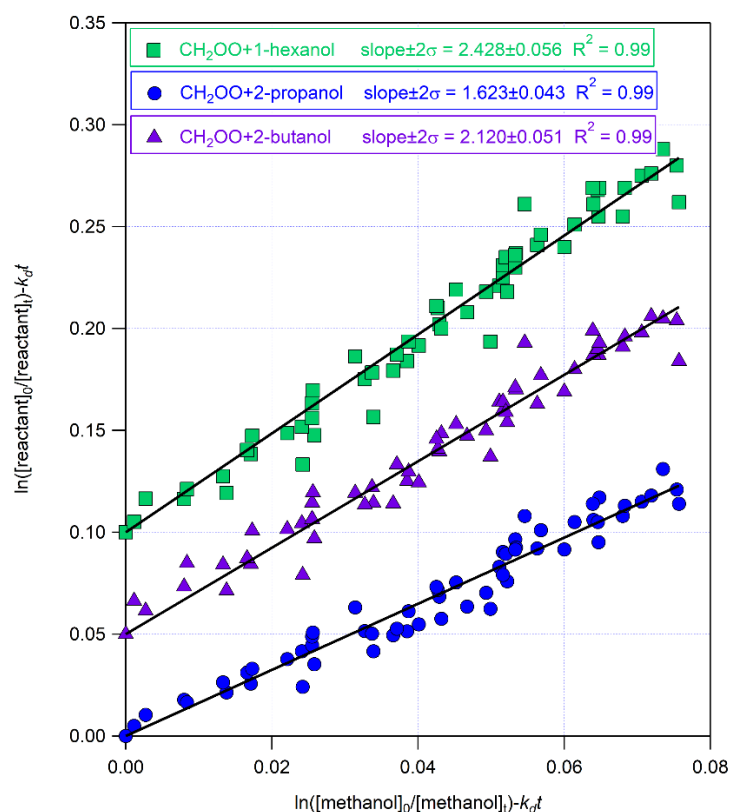


Figure 3-9. Relative rate plot from which kinetics were obtained in the *reactivity phase* of the experiment shown in Figure 3-8. k_d in the axis label refers to the total first-order loss rate constant (dilution + wall loss + instrumental stability), determined from the *stabilization phase*. Linear regression slopes with $\pm 2\sigma$ uncertainties are shown for each fit; these correspond directly to the slope values listed in Table 3-1. Because of the similarity in rate coefficients, relative rate traces are offset by 0.05 (for 2-butanol) and 0.10 (for 1-hexanol) in the y-axis.

By running the model, we found that the exceptionally high reactivity of CH_2OO with acids ensures that it reacts almost exclusively with the acid, with negligible competition from other components in the system, such as carbonyls and peroxidic products. The effect of product accumulation only began to be significant as the acid neared complete consumption. Hence, we could easily simulate the consumption of acids and O_3 (as well as ethene), which can be reflected from the excellent agreement between experimental traces and the output of our explicit model. Moreover, the time dependences of masses of the hydroperoxide and mixed anhydride products mirror the consumption of acid reactants, indicating that these species are produced in the initial chemical step, rather than in a more convoluted secondary process.

By contrast, in the alcohol case, the accumulation of products leads to an increased complexity. The use of higher ethene concentrations, intended to boost SCI production and compensate for the lower reactivity of alcohols, simultaneously resulted in a substantial accumulation of carbonyl co-products (formaldehyde in this case, see detailed mechanism above). Through simulation, CH₂OO competes between reacting with alcohols and with HCHO, as previously discovered by (Docherty et al., 2004), and this competition intensifies over time. Applying the latest rate coefficient of $3.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the CH₂OO + HCHO reaction reported by (Enders et al., 2024), in competition with insertion into alcohols, CH₂OO will also undergo cycloaddition with HCHO to form a secondary ozonide (SOZ, 1,2,4-trioxilane in this case). (Vereecken and Francisco, 2012b) have noted that the fate of SOZ remains largely unknown, with detailed theoretical studies so far limited to fluorinated SOZ analogs (Ljubić and Sabljčić, 2005), which exhibit high decomposition barriers. In our system, the compact structure of 1,2,4-trioxilane, likely formed with excess internal energy, may allow for partial reversibility. To reconcile the modelled decay of alcohols with the experimental observations, we incorporated a small reversible reaction of SOZ dissociating back into CH₂OO and HCHO. No direct evidence of a stabilized SOZ was detected in our measurements, suggesting that alternative decomposition pathways dominate, most notably, cleavage to methylene bis-oxy or dioxirane. The former is known to rapidly decompose to OH + HCO via a “hot-acid” mechanism (Kroll et al., 2002), while the behaviour of dioxirane remains less understood. Nevertheless, assuming reactivity with saturated organic species such as alcohols, as reported by (Mello et al., 1989), it would likely be scavenged efficiently by the large excess of cyclohexane present in the system, thereby suppressing unwanted secondary oxidation. Reactions with HO₂ can also be neglected, as their rate coefficients with alcohols under ambient conditions are extremely low. As in the case of the acids, evidence of hydroperoxide (and associated formate) production is clear in the PTR-MS measurements, although to a lesser extent because of the reduced conversion of reactant molecules in these experiments. Interestingly, hydroperoxide production appears to be more efficient in the second injection of ethene, which may indicate that there is a difference in the energy partitioning of SCIs later on in the experiment.

3.3.3 Kinetic results

This study extended the relative rate technique to determine bimolecular rate coefficients for reactions between CH_2OO and compounds bearing “-C(O)OH” or “-OH” functional moieties (applicable to SCI insertion mechanism), and in total, two organic acids were measured relative to acetic acid and five alcohols were measured relative to methanol. Figure 3-10 summarizes the relative rate data obtained in this study alongside previously reported absolute rate measurements from the literature. The corresponding tabulated values can be found in Table 3-1. The complete set of relative rate plots for acid and alcohol experiments is presented in Figure 3-11 and Figure 3-12, respectively.

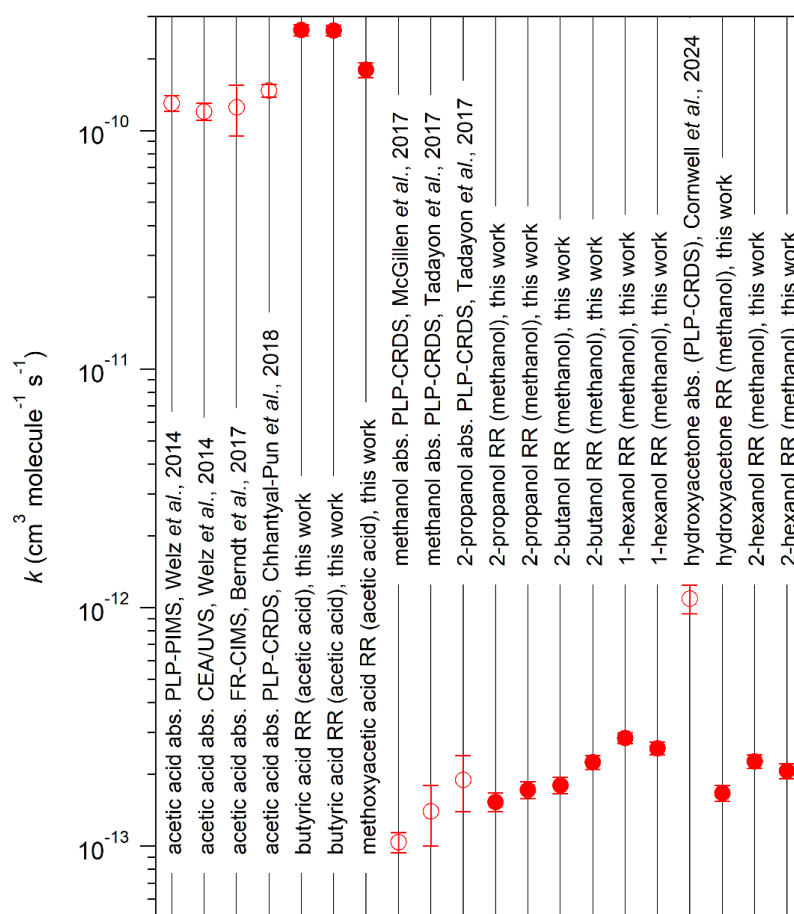


Figure 3-10. A summary of the CH_2OO relative rate (RR) coefficients obtained in this work (filled circles), with reference compounds in parentheses, together with available absolute literature measurements (open circles) at room temperature (Berndt *et al.*, 2017; Chhantyal-Pun *et al.*, 2018; Cornwell *et al.*, 2024; McGillen *et al.*, 2017; Tadayon *et al.*, 2018; Welz *et al.*, 2014). These data are available in a tabulated form in Table 3-1.

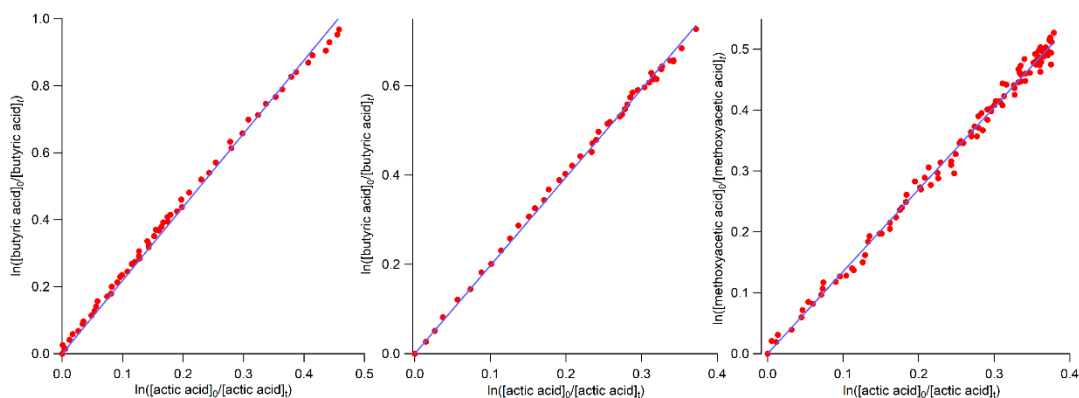


Figure 3-11. Relative rate plots for all acids studied in this work, using acetic acid as the reference compound.

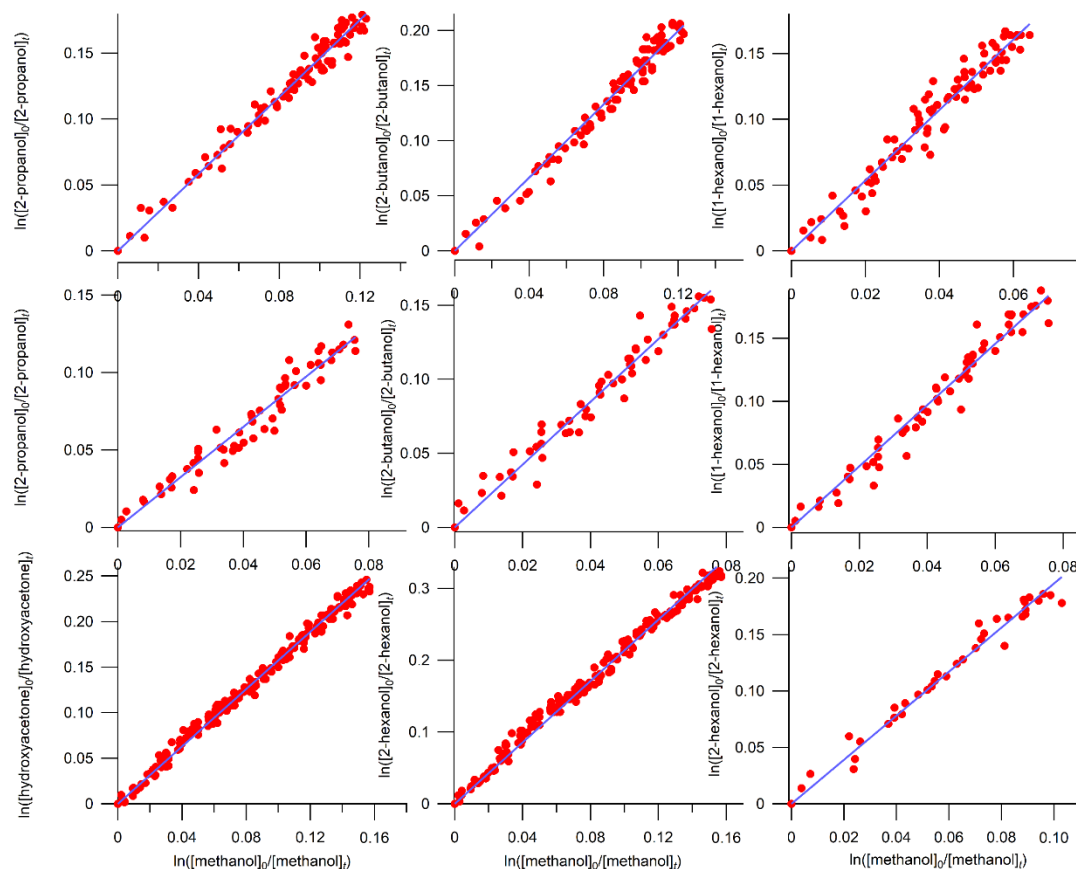


Figure 3-12. Relative rate plots for all alcohols studied in this work, using methanol as the reference compound.

As expected, all relative rate fits exhibited excellent linearity with minimal scatter. Good agreement between independent measurements indicates strong experimental reproducibility and suggests that interference from unexpected radical or heterogeneous loss processes was not a major concern.

Based on weighted averages of all measurements, we provide the following recommended rate coefficients ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for each compound in Table 3-1.

Table 3-1. Tabulated experimental results for the reactions of CH_2OO + acids/alcohols, together with literature measurements, where available.

Compound	k compound ^a	Method ^b	Reference compound	Slope ^c	k referenced ^a	T ^d	Source
acetic acid	$(1.30 \pm 0.10) \times 10^{-10}$	abs				298	(Welz et al., 2014)
	$(1.20 \pm 0.10) \times 10^{-10}$	abs				298	(Welz et al., 2014)
	$(1.25 \pm 0.30) \times 10^{-10}$	abs				295	(Berndt et al., 2017)
	$(1.47 \pm 0.09) \times 10^{-10}$	abs				293	(Chhantyal-Pun et al., 2018b)
	$(1.33 \pm 0.06) \times 10^{-10}$	<i>recommended^e</i>					
butyric acid	$(2.64 \pm 0.14) \times 10^{-10}$	RR	acetic acid	1.983 ± 0.015	$(1.33 \pm 0.06) \times 10^{-10}$	284	This work
	$(2.63 \pm 0.13) \times 10^{-10}$	RR	acetic acid	1.976 ± 0.012	$(1.33 \pm 0.06) \times 10^{-10}$	280	This work
	$(2.63 \pm 0.10) \times 10^{-10}$	<i>recommended^e</i>					
methoxy-acetic acid	$(1.80 \pm 0.13) \times 10^{-10}$	RR	acetic acid	1.350 ± 0.014	$(1.33 \pm 0.06) \times 10^{-10}$	287	This work
	$(1.80 \pm 0.13) \times 10^{-10}$	<i>recommended^e</i>					
methanol	$(1.04 \pm 0.10) \times 10^{-13}$	abs				292	(McGillen et al., 2017b)
	$(1.40 \pm 0.40) \times 10^{-13}$	abs				295	(Tadayon et al., 2018)
	$(1.06 \pm 0.10) \times 10^{-13}$	<i>recommended^e</i>					
2-propanol	$(1.53 \pm 0.14) \times 10^{-13}$	RR	methanol	1.446 ± 0.039	$(1.06 \pm 0.10) \times 10^{-13}$	295	This work
	$(1.72 \pm 0.14) \times 10^{-13}$	RR	methanol	1.623 ± 0.043	$(1.06 \pm 0.10) \times 10^{-13}$	295	This work
	$(1.90 \pm 0.50) \times 10^{-13}$	abs				295	(Tadayon et al., 2018)
	$(1.64 \pm 0.10) \times 10^{-13}$	<i>recommended^e</i>					
2-butanol	$(1.80 \pm 0.14) \times 10^{-13}$	RR	methanol	1.694 ± 0.045	$(1.06 \pm 0.10) \times 10^{-13}$	295	This work
	$(2.25 \pm 0.15) \times 10^{-13}$	RR	methanol	2.120 ± 0.051	$(1.06 \pm 0.10) \times 10^{-13}$	295	This work
	$(2.01 \pm 0.10) \times 10^{-13}$	<i>recommended^e</i>					
1-hexanol	$(2.84 \pm 0.15) \times 10^{-13}$	RR	methanol	2.680 ± 0.057	$(1.06 \pm 0.10) \times 10^{-13}$	295	This work

	$(2.57 \pm 0.16) \times 10^{-13}$	RR	methanol	2.428 ± 0.056	$(1.06 \pm 0.10) \times 10^{-13}$	295	This work
	$(2.72 \pm 0.11) \times 10^{-13}$	<i>recommended^e</i>					
hydroxy-acetone	$(1.09 \pm 0.15) \times 10^{-12}$	RR				295	This work
	$(1.67 \pm 0.13) \times 10^{-13}$	abs	methanol	1.574 ± 0.010	$(1.06 \pm 0.10) \times 10^{-13}$	282	(Cornwell et al., 2024)
	$(1.67 \pm 0.13) \times 10^{-13}$	<i>recommended^e</i>					
2-hexanol	$(2.27 \pm 0.15) \times 10^{-13}$	RR	methanol	2.139 ± 0.016	$(1.06 \pm 0.10) \times 10^{-13}$	282	This work
	$(2.07 \pm 0.15) \times 10^{-13}$	RR	methanol	1.952 ± 0.043	$(1.06 \pm 0.10) \times 10^{-13}$	294	This work
	$(2.17 \pm 0.11) \times 10^{-13}$	<i>recommended^e</i>					

^aUnits of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, errors are reported at weighted averages of reference rate constants and measured slopes.

^bMethod abbreviations: “RR” = relative rate, “abs” = absolute method. ^cMeasured slopes, errors are 2σ . ^dUnits of Kelvin.

^eRecommended values are error-weighted means, where multiple measurements are available (this work and literature values), otherwise, they represent single measurements.

A clear trend is observed across both acids and alcohols, wherein bimolecular rate coefficients tend to increase with molecular mass. For example, the rate coefficient for butyric acid is nearly twice that of acetic acid, suggesting that heavier acids may exhibit enhanced reactivity toward CH_2OO . Similar mass dependence is noted in the alcohol series. The branching effects, however, appear to play a minor role, such as the difference between 1-hexanol and 2-hexanol. The general behaviour aligns with previous studies on SCI reactions with heavier co-reactants, which have shown that increased molecular mass may enhance insertion kinetics (Chhantyal-Pun et al., 2017; Peltola et al., 2024). As noted by (Chhantyal-Pun et al., 2018), reduced zero-point energy and vibrational coupling in lighter molecules may suppress their reactivity with CH_2OO , whereas heavier molecules offer more favourable conditions for insertion.

Notably, we did observe a discrepancy between our measured relative rate coefficient for hydroxyacetone and the reported absolute measurement by (Cornwell et al., 2024). Specifically, our determination of $(1.67 \pm 0.13) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is significantly lower than the absolute value of $1.02 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by (Cornwell et al., 2024), differing by more than a factor of six. By comparison, our result is more consistent with expectations for alkyl-substituted alcohols or ketones of similar structure and reactivity, as supported by earlier work (McGillen et al., 2017; Taatjes

et al., 2012; Tadayon et al., 2018). While it would be presumptuous to dismiss the accuracy of Cornwell et al.'s measurements outright, we hypothesize that the discrepancy arises from the inherent challenges in working with low-volatility compounds in flow-based absolute kinetic setups. Such challenges include inefficient vaporization, enhanced wall interactions, possible dimerization, or even aerosol formation, all of which could complicate the interpretation of decay kinetics or lead to high rate constants.

3.3.4 Concerns from other oxidants

To quantitatively interpret the observed reactivity of CH_2OO with acids/alcohols, it is important to consider the chemical complexity inherent in ethene ozonolysis.

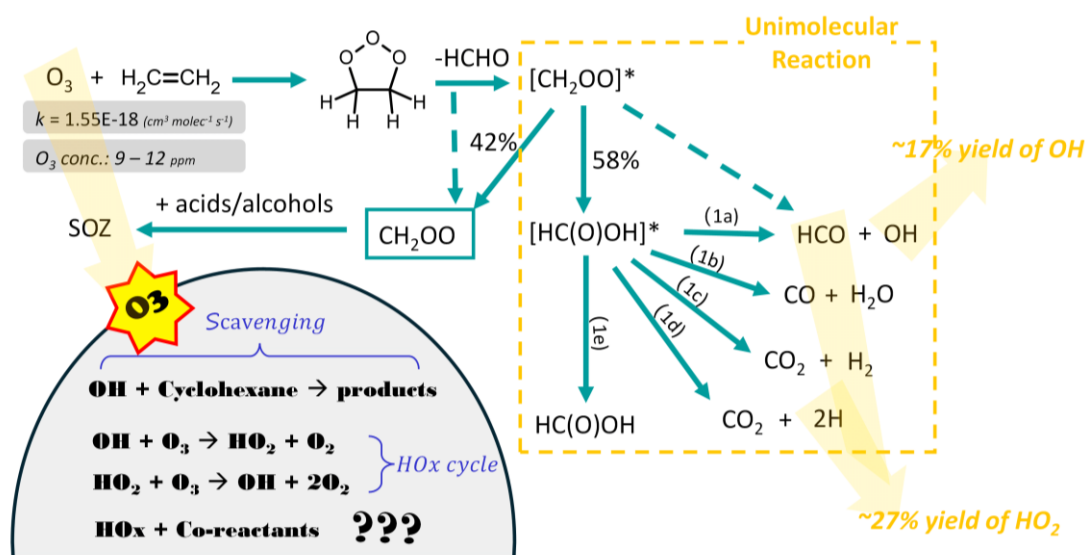


Figure 3-13. Reaction scheme illustrating the ozonolysis of ethene, yielding CH_2OO and formaldehyde. The initial reaction pathway and branching ratio are based on IUPAC recommendation, with 42% of the channel leading to CH_2OO formation and 58% resulting in the formation of vibrationally excited HC(O)OH^* . The unimolecular decomposition of these intermediates leads to a variety of products including HCO , CO , CO_2 , and H_2 , and contributes to secondary radical production with estimated yields of ~17% for OH and ~27% for HO_2 . The diagram also highlights potential HO_x propagation cycles that may arise in relative rate experiments due to high ozone input.

As illustrated in Figure 3-13, the dissociation of CIs proceeds via two major channels: approximately 42% of the total reaction flux leads to the formation of SCIs (target oxidant in this study), while the remaining 58% isomerize to vibrationally excited HC(O)OH^* , which would undergo further unimolecular decomposition, generating a range of radical and stable products including OH, HO_2 , HCO, CO, and CO_2 (IUPAC, 2025). These branching pathways imply that CH_2OO is not the only reactive oxidant produced *in situ*, and that secondary radical formation (e.g., OH and HO_2) may occur alongside.

As mentioned above, high O_3 concentrations for compensating the slow reaction with ethene would in practice accelerate ozonolysis and maximize SCI yield. However, it also presents a potential complication: excess ozone can engage in secondary reactions, including those with OH radicals, even when an OH scavenger (cyclohexane) is present in large excess. Specifically, $\text{OH} + \text{O}_3$ can regenerate HO_2 , which then reacts with ozone to recycle OH. Although reactions, such as $\text{OH} + \text{HO}_2$ and $\text{HO}_2 + \text{HO}_2$, could represent net sinks of HO_x under dark conditions, the possibility of radical propagation cycles introduces a potential source of reactivity that may compete with SCI kinetics.

To investigate this in detail, we constructed a near-explicit box model of the chamber experiments in order to assess other possible loss processes (e.g., OH, HO_2 , RO_2 and RO). By tagging the reactant loss with respect to these oxidants, we were able to estimate their relative contribution to the loss of our compounds in the relative rate. A summary of these results is provided below for the experiments shown in Figure 3-14 and Figure 3-15.

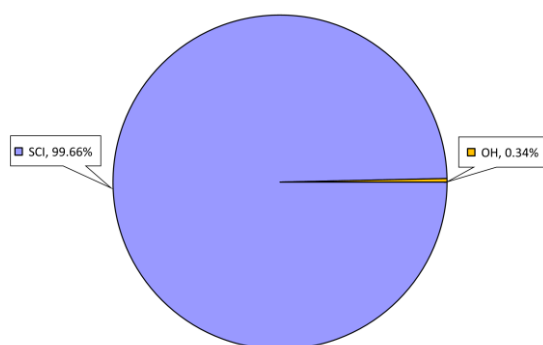


Figure 3-14: Contributions of the various oxidants (SCI and OH) to the decay of butyric acid by the end of the relative rate measurement shown in Figure 3-6. The contribution of other oxidants (e.g. RO_2 , RO and HO_2) is negligible $<0.0001\%$.

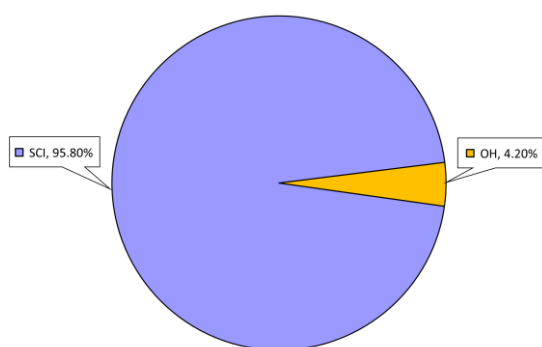


Figure 3-15: Contributions of the various oxidants (SCI and OH) to the decay of 1-hexanol by the end of the relative rate measurement shown in Figure 3-8. The contribution of other oxidants (e.g., RO₂, RO and HO₂) is negligible <0.0001%.

From these model simulations, it is clear that the contribution of other oxidants is negligible for butyric acid and is of only minor importance for 1-hexanol. It should be noted that very little is known about the rate coefficient of RO₂ + acids/alcohols and RO + acids/alcohols under ambient conditions. Therefore, we based our modelled rate coefficients on the review of (Tsang, 1987), who provide a value of $3.08 \times 10^{-22} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K for the analogous system CH₃OO + CH₃OH, and a value of $5.38 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K for the reaction CH₃O + CH₃OH. In the absolute absence of information regarding the reaction with organic acids, we assume the same rate coefficient in this case. Based upon these, the modelled contributions from RO₂-based losses were 0.016% for butyric acid and 0.366% for 1-hexanol. Similarly, RO-based losses contributed just 0.000030% and 0.00071% for butyric acid and 1-hexanol, respectively. Incidentally, the reaction with OH is found to be more important, which can contribute up to 4% in the case of 1-hexanol. This is a possible consequence of efficient HO_x recycling in the chamber. It should be noted that these represent the worst-case scenarios in the examples in Figures 3-14 and Figure 3-15, since these species have larger OH rate coefficients than their smaller homologues. We also investigated possible contributions from HO₂ radicals in these systems, but it was found to be negligible (<0.00000001% contribution in both cases).

Additionally, Figure 3-16 and Figure 3-17 present the relative lifetimes of acid/alcohol reactants with respect to different oxidants across the course of the experiment. These simulations further illustrate that SCI chemistry consistently displays the shortest lifetime. Even under more challenging cases such

as 2-butanol and 1-hexanol, the lifetime with respect to OH remains at least ten times longer than that with respect to SCI. This clearly supports the conclusion that CH_2OO is the dominant oxidant and that its kinetics can be reliably isolated using the relative rate method.

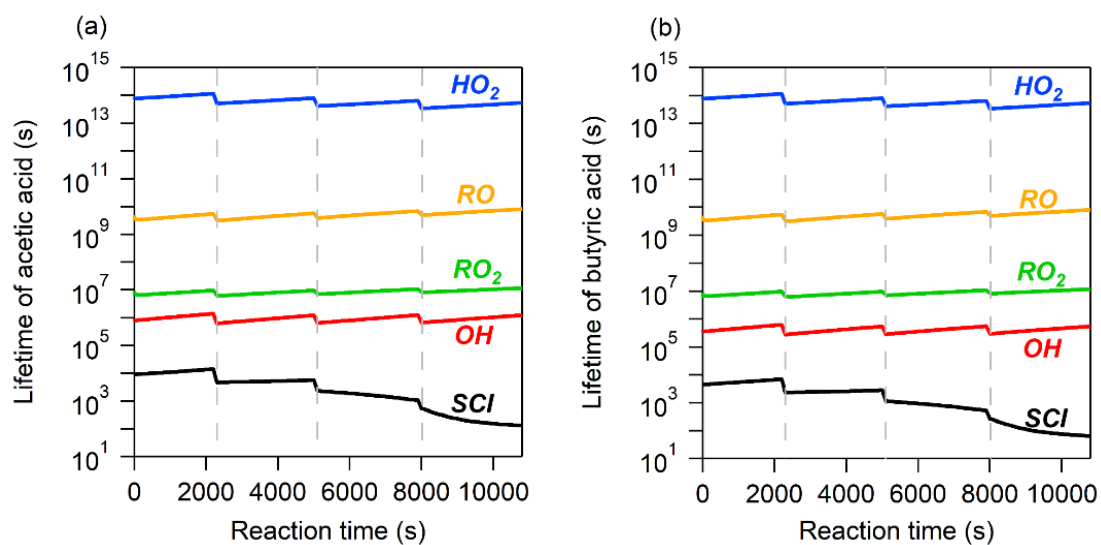


Figure 3-16. Modeled time-resolved lifetimes of (a) acetic acid and (b) butyric acid with respect to key oxidants (SCI , OH , RO_2 , RO , HO_2), corresponding to the reactivity phase and product observation phase shown in Figure 3-6. The vertical discontinuities in the curves correspond to discrete ethene injection events, which initiate new SCI production.

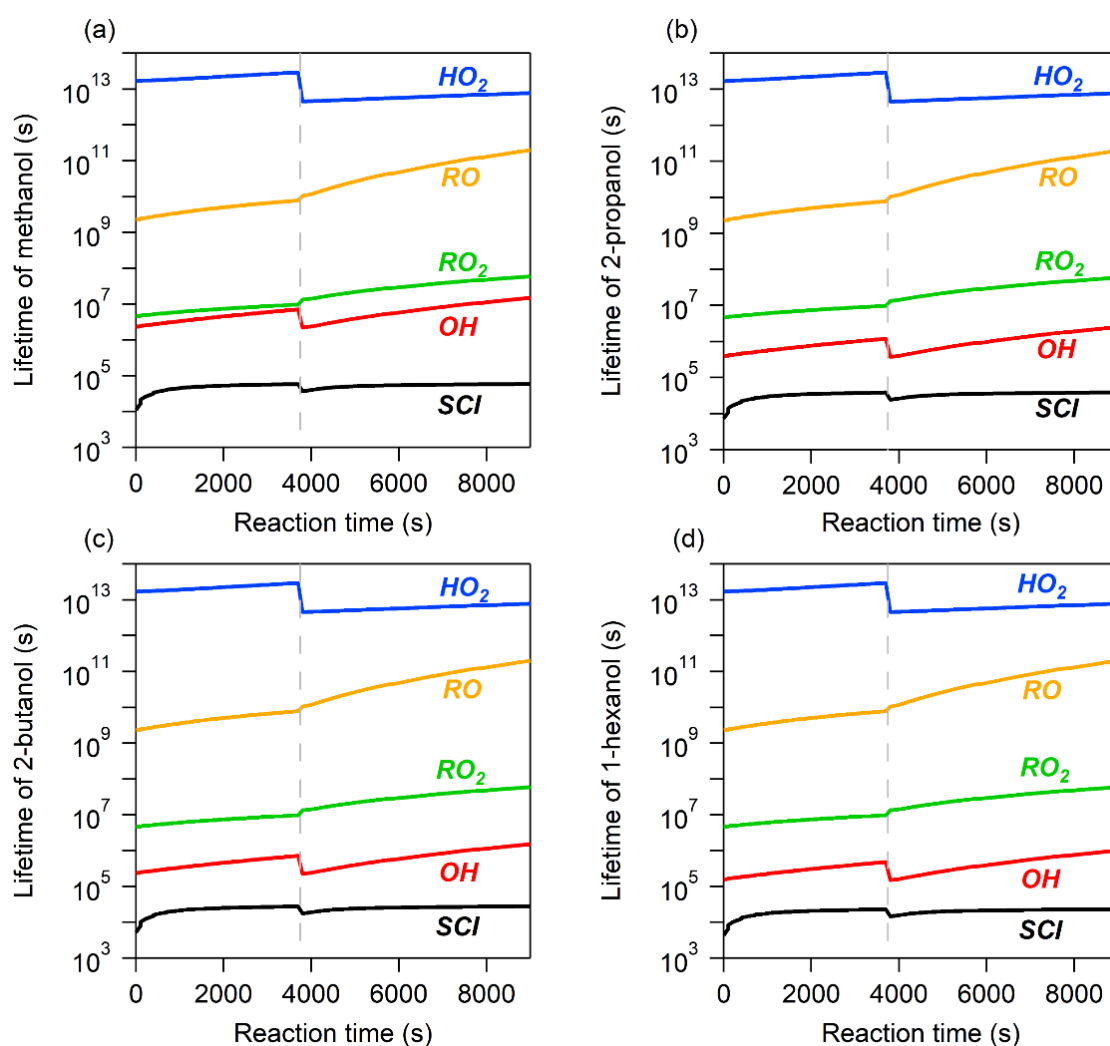


Figure 3-17. Modeled time-resolved lifetimes of (a) methanol, (b) 2-propanol, (c) 2-butanol, and (d) 1-hexanol with respect to key oxidants (SCI, OH, RO₂, RO, HO₂), corresponding to the reactivity phase and product observation phase shown in Figure 3-8. The vertical discontinuities in the curves correspond to discrete ethene injection events, which initiate new SCI production.

3.3.5 Application to more compounds

CH₂OO is the simplest and the most extensively studied Criegee intermediate, and despite its reactions with acids are nearly barrierless, its kinetic characterization toward acids in the database is still largely limited to very small acids such as formic acid, acetic acid and trifluoroacetic acid (IUPAC, 2025). Based

on these absolute rate coefficients, we applied the chamber-based relative rate approach to a broader range of organic acids.

Table 3-2. Tabulated experimental results of the extended measurements for the reactions of CH₂OO + acids.

Target compound	k^a	Slope ^b	k ref	Ref source	Reference	Radical scavenger	T ^c
propionic acid	$(2.78 \pm 0.28) \times 10^{-10}$	2.136 ± 0.027	1.30×10^{-10}	(IUPAC, 2025)	acetic acid	cyclohexane	293
propionic acid	$(2.21 \pm 0.33) \times 10^{-10}$	0.840 ± 0.003	2.63×10^{-10}	(Wang et al., 2025)	butyric acid	cyclohexane	291
isobutyric acid	$(2.32 \pm 0.23) \times 10^{-10}$	1.781 ± 0.012	1.30×10^{-10}	(IUPAC, 2025)	acetic acid	cyclohexane	299
isobutyric acid	$(2.44 \pm 0.24) \times 10^{-10}$	1.877 ± 0.010	1.30×10^{-10}	(IUPAC, 2025)	acetic acid	cyclohexane	291
valeric acid	$(2.83 \pm 0.28) \times 10^{-12}$	2.178 ± 0.008	1.30×10^{-10}	(IUPAC, 2025)	acetic acid	cyclohexane	293
valeric acid	$(2.76 \pm 0.41) \times 10^{-10}$	1.048 ± 0.003	2.63×10^{-10}	(Wang et al., 2025)	butyric acid	cyclohexane	291
isovaleric acid	$(2.56 \pm 0.30) \times 10^{-10}$	2.279 ± 0.014	1.30×10^{-10}	(IUPAC, 2025)	acetic acid	cyclohexane	291
pivalic acid	$(2.70 \pm 0.27) \times 10^{-10}$	2.074 ± 0.029	1.30×10^{-10}	(IUPAC, 2025)	acetic acid	cyclohexane	288
pivalic acid	$(2.44 \pm 0.24) \times 10^{-10}$	1.877 ± 0.010	1.30×10^{-10}	(IUPAC, 2025)	acetic acid	cyclohexane	288
Pyruvic acid	$(1.84 \pm 0.28) \times 10^{-11}$	1.862 ± 0.022	9.87×10^{-12}	(Cornwell et al., 2023)	biacetyl	cyclohexane	306
pyruvic acid	$(2.07 \pm 0.31) \times 10^{-11}$	1.751 ± 0.027	1.18×10^{-11}	(Cornwell et al., 2023)	biacetyl	cyclohexane	293
2-oxobutanoic acid	$(2.48 \pm 0.37) \times 10^{-11}$	2.025 ± 0.017	1.22×10^{-11}	(Cornwell et al., 2023)	biacetyl	cyclohexane	290
2-oxobutanoic acid	$(2.74 \pm 0.41) \times 10^{-11}$	2.606 ± 0.021	1.05×10^{-11}	(Cornwell et al., 2023)	biacetyl	cyclohexane	301
2-oxobutanoic acid	$(2.49 \pm 0.38) \times 10^{-11}$	2.125 ± 0.052	1.17×10^{-11}	(Cornwell et al., 2023)	biacetyl	cyclohexane	293
3-methyl-2-oxobutanoic acid	$(2.93 \pm 0.44) \times 10^{-11}$	2.786 ± 0.027	1.05×10^{-11}	(Cornwell et al., 2023)	biacetyl	cyclohexane	301
3-methyl-2-oxobutanoic acid	$(2.86 \pm 0.43) \times 10^{-11}$	2.440 ± 0.051	1.17×10^{-11}	(Cornwell et al., 2023)	biacetyl	cyclohexane	293

^aUnits of cm³ molecule⁻¹ s⁻¹, errors are reported at weighted averages of reference rate constants and measured slopes.

^bMeasured slopes, errors are 2 σ . ^cUnits of Kelvin.

Each individual measurement yielded very good linearity and excellent consistency between repeated experiments. Table 3-2 summarizes the rate coefficients and corresponding experimental parameters for the reactions of CH₂OO with a series of linear, branched, and oxo-substituted carboxylic acids. The rate coefficients of linear acids (such as propionic acid and valeric acid) are generally higher than that of acetic acid, confirming observations in earlier sections that increasing carbon chain length/mass enhances the insertion reactivity by CH₂OO (Wang et al., 2025). In contrast, branched acids such as isobutyric acid, isovaleric acid, and pivalic acid exhibited slightly lower rate coefficients than their linear analogues, indicating that branching exerts a minor negative effect on Criegee kinetics (Wang et al., 2025).

In the case of oxo-substituted carboxylic acids, we observed that the rate coefficients were significantly lower than those of linear or branched acids, typically by about an order of magnitude. For example, in the case of pyruvic acid, we obtained a rate coefficient of approximately $2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is consistent with the SAR-based estimation reported by Chhantyal-Pun et al., (2018). Enders et al., (2025) investigated the kinetics of CH₂OO with pyruvic acid over the temperature range of 275-375 K using an absolute rate method, and found that the rate coefficient exhibited non-Arrhenius behavior, with a value of $(1.95 \pm 0.12) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at room temperature, in good agreement with our results. This reduced reactivity is likely due to the strong intramolecular hydrogen bonding in pyruvic acid, which effectively suppress the typical insertion pathway and forces the reaction to proceed mainly via the higher-barrier 1,3-cycloaddition (Chhantyal-Pun et al., 2018; Enders et al., 2025). A similar effect is also observed for other α -keto acids, such as 2-oxobutanoic acid and 3-methyl-2-oxobutanoic acid.

To further extend the applicability of our method, we also employed the ozonolysis of tetramethylethylene (TME) to generate acetone oxide, which served as a single oxidant for studying its reactions with several acids. As a highly symmetric alkene, TME undergoes ozonolysis to produce an energy-rich POZ, which rapidly decomposes to yield an excited Criegee intermediate, $[(\text{CH}_3)_2\text{COO}]^*$, and acetone, $\text{CH}_3\text{C}(\text{O})\text{CH}_3$. The energized $[(\text{CH}_3)_2\text{COO}]^*$ can be collisionally quenched to form the SCl, $(\text{CH}_3)_2\text{COO}$, which then participates in the target reactions. The yield of $(\text{CH}_3)_2\text{COO}$ at 1 bar is reported

to be $38 \pm 10\%$ (IUPAC, 2025). Notably, both the excited and stabilized $(\text{CH}_3)_2\text{COO}$ are predicted to produce OH radicals with a high yield ($93 \pm 14\%$), together with an acetonyl radical, $\text{CH}_3\text{C}(\text{O})\text{CH}_2$, as a coproduct, through unimolecular decomposition of the vinyl hydroperoxide intermediate via β -hydrogen abstraction (IUPAC, 2025).

An excess of cyclohexane ($6.34\text{--}7.61 \times 10^{14}$ molecules cm^{-3}) was added to suppress the OH concentration, while the acetonyl radical is expected under atmospheric pressure to react rapidly with O_2 to form a peroxy radical, subsequently yielding multiple secondary products. Since the reactions of $(\text{CH}_3)_2\text{COO}$ with acids are extremely fast (e.g., with acetic acid, $k = 3.1 \times 10^{-10}$ $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), the reactions of OH and RO_2 radicals with acids are negligible compared to SCI under these conditions. However, in the case of alcohols or other compounds with relatively low reactivity toward SCIs, significant uncertainties from OH side reactions are anticipated.

Table 3-3. Tabulated experimental results of the extended measurements for the reactions of $(\text{CH}_3)_2\text{COO} + \text{acids}$.

Target compound	k^a	Slope ^b	k ref	Ref source	Reference	Radical scavenger	T ^c
butyric acid	$(3.68 \pm 0.37) \times 10^{-10}$	1.188 ± 0.008	3.10×10^{-10}	(IUPAC, 2025)	acetic acid- d_3	cyclohexane	305
butyric acid	$(3.71 \pm 0.37) \times 10^{-10}$	1.197 ± 0.010	3.10×10^{-10}	(IUPAC, 2025)	acetic acid- d_3	cyclohexane	297
isobutyric acid	$(3.23 \pm 0.32) \times 10^{-10}$	1.042 ± 0.004	3.10×10^{-10}	(IUPAC, 2025)	acetic acid- d_3	cyclohexane	303
isovaleric acid	$(3.64 \pm 0.37) \times 10^{-10}$	1.175 ± 0.008	3.10×10^{-10}	(IUPAC, 2025)	acetic acid- d_3	cyclohexane	303

^aUnits of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, errors are reported at weighted averages of reference rate constants and measured slopes.

^bMeasured slopes, errors are 2σ . ^cUnits of Kelvin.

Since the reaction rate coefficient of TME with ozone (1.10×10^{-15} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is relatively fast compared to that of ethene (1.55×10^{-18} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), the required O_3 input (7.38×10^{13} molecules cm^{-3}) in the experiments could be reduced compared with ethene experiments. The liquid TME sample was maintained in a 40°C water bath, and a constant flow of zero air was passed over it to carry the vapor continuously into the chamber, where ozonolysis was initiated. Table 3-3 summarizes the kinetic results obtained so far, in which we again observed satisfactory linearity in relative rate plots. In these experiments, we used deuterated acetic acid (CD_3COOH) instead of regular acetic acid as the reference compound, because the acetic acid signal (m/z 78.056) was subject to

interference from other byproducts, likely associated with chain reactions initiated during TME ozonolysis. The SCI reactions proceed primarily via insertion at the –OOH site of the acid, and in such fast, barrierless reactions (Chhantyal-Pun et al., 2017), no measurable kinetic difference is expected between CD_3COOH and CH_3COOH . First, hydrogen and deuterium have nearly identical bond lengths and steric volumes, and thus steric hindrance effect can be neglected (Bigeleisen and Wolfsberg, 1957). Second, their electron donating properties are virtually identical, and thus the electron density at the reactive site is essentially unaffected (Bigeleisen and Wolfsberg, 1957). The experimental results show that, similar to the $\text{CH}_2\text{OO} + \text{acid}$ reactions, we also observed a clear mass dependence in the $(\text{CH}_3)_2\text{COO}$ insertion reactions, while branching led to slightly reduced rate coefficients.

3.4 Atmospheric implications

The kinetic data obtained in this study provide new insights into the atmospheric relevance of CH_2OO as a reactive oxidant toward oxygenated volatile organic compounds (OVOCs), particularly organic acids and alcohols. While SCIs have been recognized as significant oxidants in atmospheric chemistry, quantitative understanding of their bimolecular reactivity has remained incomplete, as illustrated in Figure 3-16. This box plot compiles all experimentally determined rate coefficients available in the database from (McGillen et al., 2020). Given the abundance of biogenic alkene emissions and the diversity of Criegee intermediates that they can generate, the existing experimental coverage of SCI kinetics is disproportionately sparse, substantially limiting the exploration of subsequent ozonolysis processes.

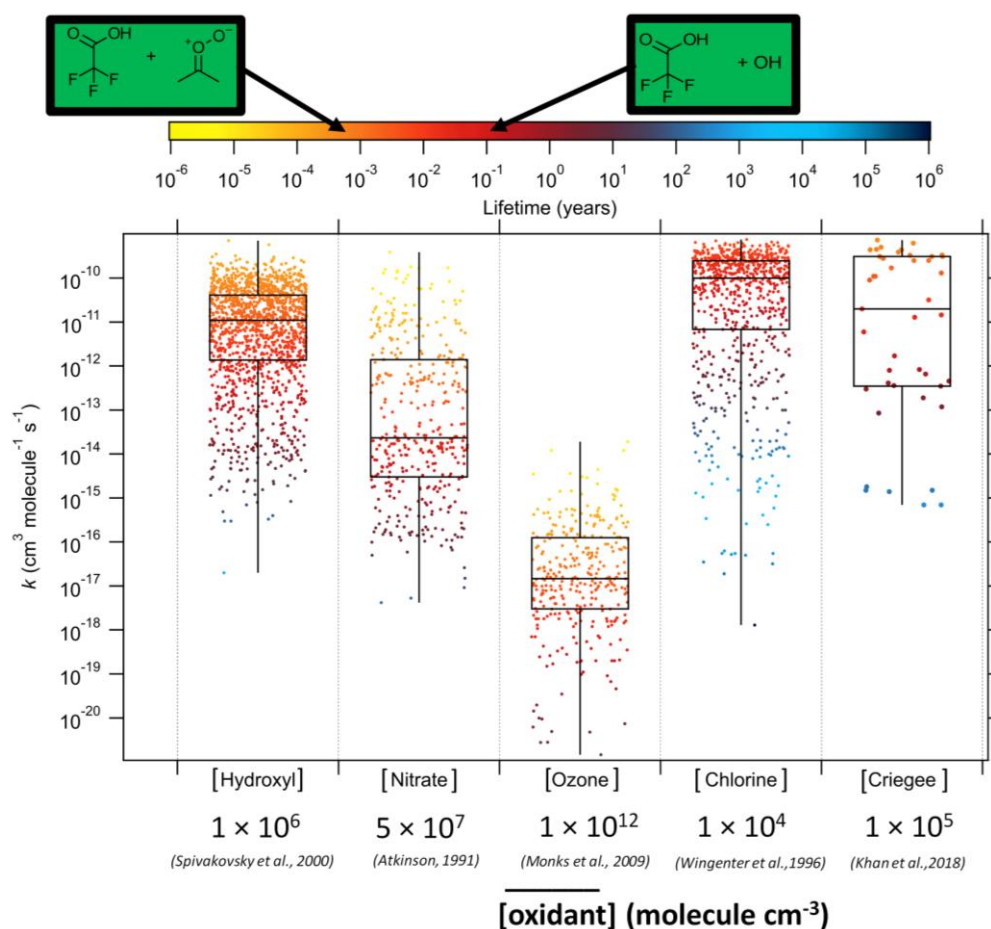


Figure 3-16. Box plot of rate coefficients (k , $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) in natural logarithm for the reactions of organic compounds reacting with five major atmospheric oxidants: OH, NO_3 , O_3 , Cl and Cls. All data are compiled from (McGillen et al., 2020). Each dot represents an individual kinetic measurement. The colorbar indicate the atmospheric lifetime (in years), which is determined using the expression $\tau = (1/[\text{oxidant}])$, where the global average oxidant concentrations are adopted from the literature accordingly (Khan et al., 2018; Monks et al., 2009; Spivakovsky et al., 2000; Wayne et al., 1991; Wingenter et al., 1996). The green areas show an example of lifetime for trifluoroacetic acid with OH and Cls to illustrate oxidant-specific fate.

From another perspective, the boxplot incorporates a colour bar to represent atmospheric lifetimes of each compound using the expression $\tau = (1/[\text{oxidant}])$. Note that the assumed [oxidant] can vary depending on the time of the day, the amount of the sunlight or the geographic location, and we only provide a global average concentration for this comparison.

Interestingly, in some cases, compounds with long atmospheric lifetimes toward OH (e.g., trifluoroacetic acid) display markedly shorter lifetimes toward Criegee intermediates. Typically, when

considering the reactivity of oxidants like OH, the dominant controlling factors are the strength of the O–H bond and how easily it can form a Van der Waals complex to proceed to reaction (Seinfeld, 2016). By contrast, Criegee intermediates follow a distinct mechanism via a R-H bond insertion or a cycloaddition that do not appear to be governed by these factors, and are often barrierless or nearly so (Chhantyal-Pun et al., 2020, 2018b). This explains the lack of correlation ($R^2 = 0.11$) between OH and Criegee intermediate rate coefficients, as observed in Figure 3-17.

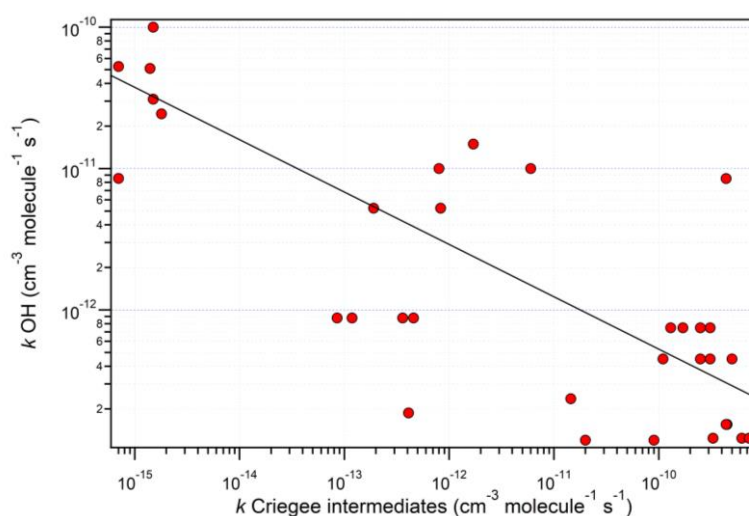


Figure 3-17. Correlation between bimolecular rate coefficients (k , $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) for the same set of organic compounds reacting with hydroxyl radicals and stabilized Criegee intermediates. Each red point represents a molecule for which both OH and Criegee intermediate rate coefficients are available.

Product observations (e.g., hydroperoxides, anhydrides and esters) provide complementary evidence supporting the feasibility of the insertion mechanism, and their accumulation may indicate a progressive transformation toward lower-volatility species. These hydroperoxides, in the gas-phase, may undergo further decomposition processes such as oxidation, photolysis or thermal decomposition, although this subsequent evolution remains poorly constrained. More importantly, the insertion reaction effectively incorporates additional carbon and oxygen atoms into molecules, increasing molecular weight and polarity, thereby enhancing their propensity to partition into the condensed phase. In the particle phase, these compounds can serve as precursors to hydrogen peroxide, hydroxyl radicals, or alkoxy species, or act directly as oxidants themselves, providing a

source of secondary oxidation. Recent field observations by Caravan et al., (2024) in the Amazon rainforest, which tracked oligomeric products arising from CH_2OO and formic acid reactions, suggesting that Criegee intermediate oligomerization can proceed even under humid conditions. This finding challenges the prevailing assumption that water dominates SCI removal under atmospheric conditions. It also suggests that the role of Criegee intermediates or other yet-uncharacterized oxidative mechanisms, may have been significantly underestimated in current atmospheric models. A more comprehensive analysis of hydroperoxide formation and their potential fate in gas-phase oxidation will be discussed in detail in Chapter 4.

3.5 Conclusion

To summarize, we presented and validated a chamber-based relative rate technique for determining the bimolecular reactivity of stabilized Criegee intermediate, using CH_2OO as a prototypical example. By employing a highly symmetrical alkene (ethene) as the precursor, we ensured the formation of a single, well-defined SCI species, which greatly simplified the mechanistic interpretation and kinetic analysis. This methodology was systematically applied to two representative classes of atmospheric compounds: carboxylic acids and alcohols, which differ markedly in reactivity. The results demonstrate that this technique reliably captures relative rate coefficients even across a wide range of reaction rates (spanning over three orders of magnitude), supported by both model simulations and product observations. Under our experimental conditions, CH_2OO dominates the reactive budget, with negligible contributions from HO_x or RO_x radicals. This ensures the chemical selectivity for extracting accurate bimolecular rate coefficients through relative decay analysis. A notable feature of the relative rate experiments is that the modelled concentrations of SCI are up to 10^6 times lower than those typically used in absolute measurements. Likewise, although the concentrations of co-reactants vary in this study, they can be reduced by $\geq 10^4$ -fold or more compared to those required for absolute methods (e.g. McGillen et al., 2017). This extends the reaction timescale by a factor of 10^6 , enabling access to a fundamentally different experimental regime achievable in chambers (see Figure 3-18).

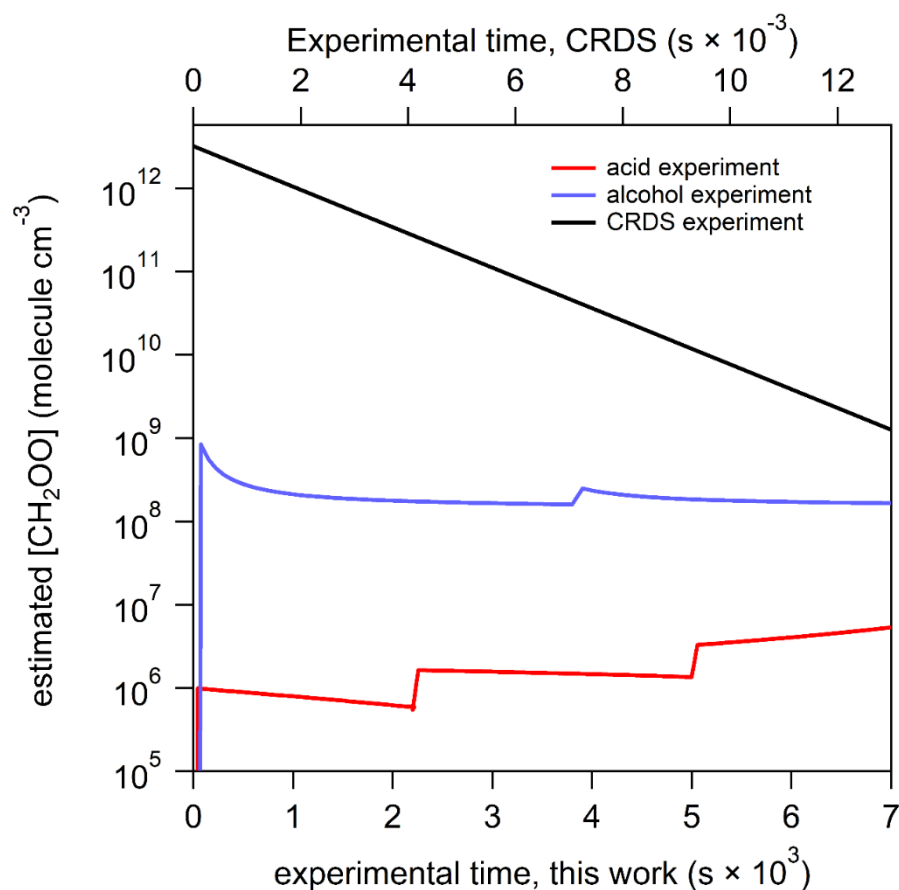


Figure 3-18: Modeled SCI concentrations in these experiments compared with the much higher concentrations calculated for absolute measurements. These traces represent the same experiments that are depicted in Figures 3-6 and 3-8, with the inflections marking the points at which ethene was introduced to the system.

This method opens new opportunities to study co-reactants with lower volatility and reactivity that are typically inaccessible by absolute techniques. These experiments allow laboratories without dedicated apparatuses for making absolute measurements, e.g., pulsed-laser photolysis–cavity ring down spectroscopic systems, to make relative measurements in chamber facilities, adding to the repertoire of accessible experiments. Nonetheless, the parameter space of SCI bimolecular reactions remains sparsely mapped and still relies on accurate absolute measurements for references. Relative measurements represent an invaluable component to kinetic database for other oxidants (e.g. OH, Cl and NO₃), and we anticipate the same rule will come to apply to SCI reactions.

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Appendices: Chapter 3

Table A3-1. Details of reactions contained within the numerical simulations of experimental time series.

#	Reactions	Rate coefficient	Reference	Comment
In the case of acid				
R1	$C_2H_4 + O_3 \rightarrow CH_2OO + HCHO$	6.51×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC5.pdf
R2	$C_2H_4 + O_3 \rightarrow HC(O)OH + HCHO$	1.09×10^{-19}	(Leather et al., 2012)	HC(O)OH yield under dry conditions
R3	$C_2H_4 + O_3 \rightarrow OH + HCHO + HCO$	2.64×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC5.pdf
R4	$C_2H_4 + O_3 \rightarrow 2H + HCHO$	4.50×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC5.pdf
R5	$C_2H_4 + O_3 \rightarrow \text{Products} + HCHO$	7.75×10^{-20}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC5.pdf
R6	$HCO + O_2 \rightarrow CO + HO_2$	5.20×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/R_Oxygen10.pdf
R7	$H + O_2 \rightarrow HO_2$	1.00×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx2.pdf
R8	$CH_2OO + HCHO \rightarrow FSOZ$	3.48×10^{-12}	(Enders et al., 2024)	
R9 ^a	$CH_2OO + n\text{-}CH_3(CH_2)_2C(O)OH \rightarrow C_3H_7C(O)OCH_2OOH$	2.63×10^{-10}	This work	In the case of acid
R10 ^a	$CH_2OO + CH_3C(O)OH \rightarrow CH_3C(O)OCH_2OOH$	1.33×10^{-10}	This work	In the case of acid
R11	$CH_2OO + ROOH \rightarrow ROO(CH_2OO)H$	1.20×10^{-13}	(Caravan et al., 2024)	Analogy to the reaction $CH_2OO + (CH_3)_3COOH$
R12	$CH_2OO + ROO(CH_2OO)H \rightarrow ROO(CH_2OO)_2H$	1.20×10^{-13}	(Caravan et al., 2024)	Analogy to the reaction $CH_2OO + (CH_3)_3COOH$
R13	$n\text{-}C_3H_7C(O)OCH_2OOH \rightarrow C_3H_7C(O)OC(O)H + H_2O$	prompt (20%)		Fitted, assuming similar PTR-MS sensitivity with $(CH_3)_3COOH$
R14	$CH_3C(O)OCH_2OOH \rightarrow CH_3C(O)OC(O)H + H_2O$	prompt (20%)		Fitted, assuming similar PTR-MS sensitivity with $(CH_3)_3COOH$
R15	$OH + HCHO \rightarrow HCO + H_2O$	8.50×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC11.pdf
R16	$OH + O_3 \rightarrow HO_2 + O_2$	7.30×10^{-14}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx13.pdf
R17	$HO_2 + O_3 \rightarrow OH + 2O_2$	2.00×10^{-15}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx15.pdf
R18	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	1.60×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx14.pdf
R19	$OH + HO_2 \rightarrow H_2O + O_2$	1.10×10^{-10}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx11.pdf
R20	$OH + c\text{-}C_6H_{12} \rightarrow c\text{-}C_6H_{11}O_2$	6.69×10^{-12}		
R21	$c\text{-}C_6H_{11}O_2 + c\text{-}C_6H_{11}O_2 \rightarrow c\text{-}C_6H_{11}O + c\text{-}C_6H_{11}O + O_2$	8.53×10^{-15}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_26.pdf
R22	$c\text{-}C_6H_{11}O_2 + c\text{-}C_6H_{11}O_2 \rightarrow c\text{-}(CH_2)_5CO + c\text{-}C_6H_{11}OH + O_2$	2.09×10^{-14}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_26.pdf
R23	$c\text{-}C_6H_{11}O_2 + HO_2 \rightarrow c\text{-}C_6H_{11}OOH + O_2$	6.90×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC53.pdf
R24	$c\text{-}C_6H_{11}O_2 + O_3 \rightarrow c\text{-}C_6H_{11}O + O_2$	1.00×10^{-17}	(Tyndall et al., 1998)	Analogy to the reaction $CH_3OO + CH_3OO$
R25	$c\text{-}C_6H_{11}O_2 + OH \rightarrow c\text{-}C_6H_{11}O + HO_2$	8.60×10^{-11}	(Fittschen, 2019)	Analogy to the reaction $CH_3OO + OH$
R26	$c\text{-}C_6H_{11}O_2 + OH \rightarrow HO_2 + O_2$	7.00×10^{-12}	(Fittschen, 2019)	Analogy to the reaction $CH_3OO + OH$
R27	$c\text{-}C_6H_{11}O_2 + OH \rightarrow c\text{-}C_6H_{11}OOOH$	7.00×10^{-12}	(Fittschen, 2019)	Analogy to the reaction $CH_3OO + OH$
R28	$c\text{-}C_6H_{11}O + O_3 \rightarrow c\text{-}C_6H_{11}O_2 + O_2$	2.53×10^{-14}	(Albaladejo et al., 2002)	Analogy to the reaction $CH_3 + O_3$

R29	$c\text{-C}_6\text{H}_{11}\text{O} + \text{O}_2 \rightarrow c\text{-(CH}_2)_5\text{CO} + \text{HO}_2$	1.00×10^{-14}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/RO_3.pdf
R30	$\text{CH}_2\text{OO} + c\text{-C}_6\text{H}_{11}\text{OH} \rightarrow \text{ROOH}$	1.00×10^{-13}	(McGillen et al., 2020)	Analogy to the reaction $\text{CH}_2\text{OO} + \text{CH}_3\text{OH}$
R31	$\text{CH}_2\text{OO} + c\text{-(CH}_2)_5\text{CO} \rightarrow \text{SOZ}$	4.00×10^{-13}	(Cornwell et al., 2021)	Analogy to the reaction $\text{CH}_2\text{OO} + (\text{CH}_3)_2\text{CO}$
R32	$\text{CH}_2\text{OO} + \text{C}_2\text{H}_4 \rightarrow \text{SOZ}$	7.00×10^{-16}	(Buras et al., 2014)	
R33	$\text{C}_2\text{H}_4 + \text{OH} \rightarrow \text{HCHO} + \text{HCHO}$	7.80×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC3.pdf
R34	$\text{FSOZ} \rightarrow \text{CH}_2\text{OO} + \text{HCHO}$	2.00×10^{-3}		Fitted to agree with observed time-series of alcohol consumption
R35 ^a	$\text{OH} + n\text{-CH}_3(\text{CH}_2)_2\text{C(O)OH} \rightarrow \text{Prod_C4_OH}$	1.80×10^{-12}	(McGillen et al., 2020)	
R36 ^a	$\text{OH} + \text{CH}_3\text{C(O)OH} \rightarrow \text{Prod_C2_OH}$	8.00×10^{-13}	(McGillen et al., 2020)	
R37 ^a	$\text{HO}_2 + n\text{-CH}_3(\text{CH}_2)_2\text{C(O)OH} \rightarrow \text{Prod_C4_HO}_2$	1.00×10^{-22}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{HO}_2$
R38 ^a	$\text{HO}_2 + \text{CH}_3\text{C(O)OH} \rightarrow \text{Prod_C2_HO}_2$	1.00×10^{-22}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{HO}_2$
R39 ^a	$c\text{-C}_6\text{H}_{11}\text{O}_2 + n\text{-CH}_3(\text{CH}_2)_2\text{C(O)OH} \rightarrow \text{Prod_C4_RO}_2$	3.00×10^{-22}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{CH}_3\text{OO}$
R40 ^a	$c\text{-C}_6\text{H}_{11}\text{O}_2 + \text{CH}_3\text{C(O)OH} \rightarrow \text{Prod_C2_RO}_2$	3.00×10^{-22}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{CH}_3\text{OO}$
R41 ^a	$c\text{-C}_6\text{H}_{11}\text{O} + n\text{-CH}_3(\text{CH}_2)_2\text{C(O)OH} \rightarrow \text{Prod_C4_RO}$	5.38×10^{-16}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{CH}_3\text{O}$
R42 ^a	$c\text{-C}_6\text{H}_{11}\text{O} + \text{CH}_3\text{C(O)OH} \rightarrow \text{Prod_C2_RO}$	5.38×10^{-16}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{CH}_3\text{O}$
R43	$\text{OH} \rightarrow \text{wall}$	1.00×10^{-2}		Constrained from previous HELIOS characterisation experiments
R44	$\text{HO}_2 \rightarrow \text{wall}$	1.00×10^{-2}		Constrained from previous HELIOS characterisation experiments
R45	$\text{CH}_2\text{OO} \rightarrow \text{wall}$	1.00×10^{-2}		Analogy to R43
R46	$c\text{-C}_6\text{H}_{11}\text{O}_2 \rightarrow \text{wall}$	1.00×10^{-2}		Analogy to R43
In the case of alcohol				
R47 ^b	$\text{CH}_2\text{OO} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_2\text{OOH}$	1.06×10^{-13}	This work	In the case of alcohol
R48 ^b	$\text{CH}_2\text{OO} + \text{CH}_3\text{CH(OH)CH}_3 \rightarrow \text{C}_2\text{H}_4(\text{OCH}_2\text{OOH})\text{CH}_3$	1.64×10^{-13}	This work	In the case of alcohol
R49 ^b	$\text{CH}_2\text{OO} + \text{CH}_3\text{CH(OH)C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4(\text{OCH}_2\text{OOH})\text{C}_2\text{H}_5$	2.01×10^{-13}	This work	In the case of alcohol
R50 ^b	$\text{CH}_2\text{OO} + \text{CH}_3(\text{CH}_2)_5\text{OH} \rightarrow \text{C}_6\text{H}_{13}\text{OCH}_2\text{OOH}$	2.72×10^{-13}	This work	In the case of alcohol
R51 ^b	$\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{Prod_C1_OH}$	8.78×10^{-13}	(McGillen et al., 2020)	
R52 ^b	$\text{OH} + \text{CH}_3\text{CH(OH)CH}_3 \rightarrow \text{Prod_C3_OH}$	5.24×10^{-12}	(McGillen et al., 2020)	
R53 ^b	$\text{OH} + \text{CH}_3\text{CH(OH)C}_2\text{H}_5 \rightarrow \text{Prod_C4_OH}$	8.69×10^{-12}	(McGillen et al., 2020)	
R54 ^b	$\text{OH} + \text{CH}_3(\text{CH}_2)_5\text{OH} \rightarrow \text{Prod_C6_OH}$	1.30×10^{-11}	(McGillen et al., 2020)	
R55 ^b	$\text{HO}_2 + \text{CH}_3\text{OH} \rightarrow \text{Prod_C1_HO}_2$	1.00×10^{-22}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{HO}_2$
R56 ^b	$\text{HO}_2 + \text{CH}_3\text{CH(OH)CH}_3 \rightarrow \text{Prod_C3_HO}_2$	1.00×10^{-22}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{HO}_2$
R57 ^b	$\text{HO}_2 + \text{CH}_3\text{CH(OH)C}_2\text{H}_5 \rightarrow \text{Prod_C4_HO}_2$	1.00×10^{-22}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{HO}_2$
R58 ^b	$\text{HO}_2 + \text{CH}_3(\text{CH}_2)_5\text{OH} \rightarrow \text{Prod_C6_HO}_2$	1.00×10^{-22}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{HO}_2$
R59 ^b	$\text{CH}_2\text{OO} + \text{CH}_3\text{OH} \rightarrow \text{Prod_C1_RO}_2$	3.00×10^{-22}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{CH}_3\text{OO}$
R60 ^b	$\text{CH}_2\text{OO} + \text{CH}_3\text{CH(OH)CH}_3 \rightarrow \text{Prod_C3_RO}_2$	3.00×10^{-22}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{CH}_3\text{OO}$

R61 ^b	$\text{CH}_2\text{OO} + \text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_5 \rightarrow \text{Prod_C4_RO}_2$	3.00×10^{-22}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{CH}_3\text{OO}$
R62 ^b	$\text{CH}_2\text{OO} + \text{CH}_3(\text{CH}_2)_5\text{OH} \rightarrow \text{Prod_C6_RO}_2$	3.00×10^{-22}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{CH}_3\text{OO}$
R63 ^b	$\text{CH}_2\text{OO} + \text{CH}_3\text{OH} \rightarrow \text{Prod_C1_RO}$	5.38×10^{-16}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{CH}_3\text{O}$
R64 ^b	$\text{CH}_2\text{OO} + \text{CH}_3\text{CH}(\text{OH})\text{CH}_3 \rightarrow \text{Prod_C3_RO}$	5.38×10^{-16}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{CH}_3\text{O}$
R65 ^b	$\text{CH}_2\text{OO} + \text{CH}_3\text{CH}(\text{OH})\text{C}_2\text{H}_5 \rightarrow \text{Prod_C4_RO}$	5.38×10^{-16}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{CH}_3\text{O}$
R66 ^b	$\text{CH}_2\text{OO} + \text{CH}_3(\text{CH}_2)_5\text{OH} \rightarrow \text{Prod_C6_RO}$	5.38×10^{-16}	(Tsang, 1987)	Analogy to the reaction $\text{CH}_3\text{OH} + \text{CH}_3\text{O}$

^aTracking of potential side reactions involving the reactants in the acid case (butyric acid and acetic acid) was achieved by tagging the products of Reactions 9, 10 and 35–42. ^bSide reactions for the alcohol case (methanol, 2-propanol, 2-butanol, and 1-hexanol) was achieved by tagging the products of Reactions 47–66. This accounts for contributions from Criegee intermediates (SCI), hydroxyl radicals (OH), hydroperoxy radicals (HO_2), organic peroxy radicals (RO_2), and alkoxy radicals (RO). Reaction products are denoted here in the format as “Prod_[CarbonNumber]_[RadicalType]” for clarity. The respective contributions are shown in Figures 3-14 and 3-15 in the Chapter 3, Section 3.3.4.

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Chapter 4:

Exploring the gas-phase reactivities of hydroperoxides (ROOHs) toward OH, NO₃ and Criegee intermediate

4.1 Introduction

Hydroperoxides (ROOH) are a class of compounds that contains the hydroperoxyl functional group ($-\text{OOH}$), and act as crucial intermediates formed in the multigenerational oxidation of volatile organic compounds in the atmosphere. In previous chapter 3, insertion reactions of stabilized Criegee intermediates (SCIs) into various co-reactants were observed to be a reliable source of functionalized hydroperoxides produced in the degradation of alkene precursors (Wang et al., 2025). As illustrated in Figure 4-1, even a single, simple Criegee intermediate, such as formaldehyde oxide (CH_2OO) formed from ethene ozonolysis, is capable of inserting into a wide range of co-reactants (e.g., water, acids, alcohols, amines and thiols), yielding a variety of ROOHs with diverse functional groups (e.g., α -hydroxyalkyl, α -alkoxyalkyl, α -alkoxyacyl, α -hydroxyalkyl nitrate and sulfate hydroperoxides) (Chhantyal-Pun et al., 2020; Khan et al., 2018; Wang et al., 2023).

In fact, ROOHs can be formed through a multitude of oxidative mechanisms. Beyond SCI insertions, one major pathway involves the self- and cross-reactions of peroxy radicals (Hasson et al., 2004; Praske et al., 2019). Under low- NO_x conditions, bimolecular reactions between RO_2 and HO_2 radicals proceed with high branching ratios and generate a wide spectrum of ROOH products (Figure 4-1). Additionally, autoxidation pathways of RO_2 radicals can be particularly favorable in the presence of moieties that promote unimolecular hydrogen-shift (H-shift) isomerization. For instance, ethers (e.g., dimethyl ether, DME in Figure 4-1) provide relatively weak C–H bonds adjacent to oxygen atoms, lowering the activation barrier for H-shift and accelerating the propagation of oxidation chains (Vereecken and Peeters, 2010; Wang and Wang, 2016). Similarly, the presence of heteroatoms such as sulfur and nitrogen has been shown to stabilize transition states for H-shift, thereby enhancing autoxidation rates and ROOH yields (Wu et al., 2015). Starting from a major atmospheric emission precursor like isoprene, even if only following a single autoxidation route, its sequential H-shift and O_2 addition steps lead to the formation of highly complex hydroperoxides with multiple $-\text{OOH}$ groups (Berndt et al., 2019).

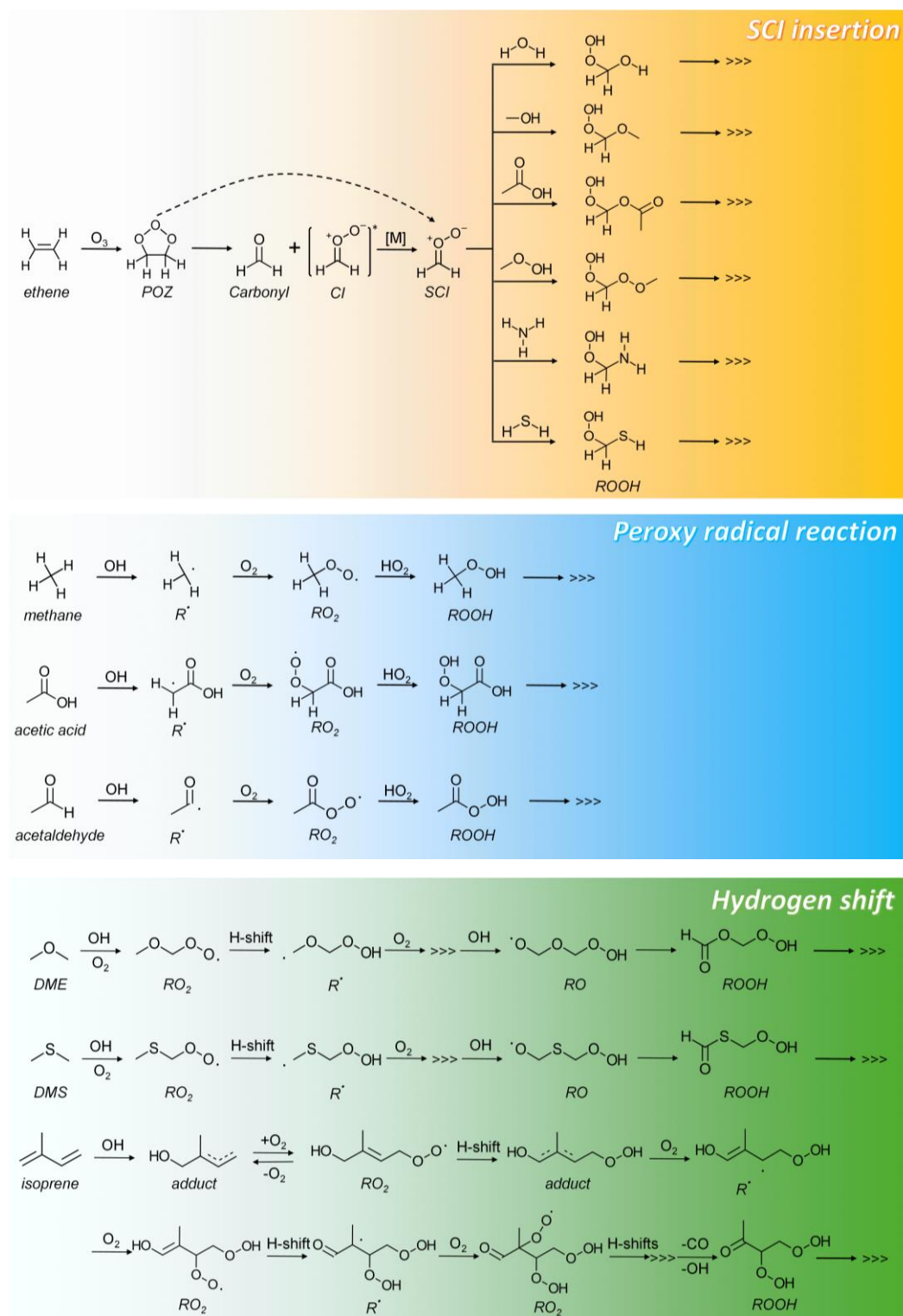


Figure 4-1. Possible atmospheric formation pathways of organic hydroperoxides (ROOH) during multigenerational oxidation cascades. Starting from simple precursors, ROOH can be formed as intermediate products via various mechanisms, including Criegee intermediate (SCI) insertion, peroxy radical (RO_2) reactions, and hydrogen-shift autoxidation.

However, many of these formation pathways have only been elucidated in recent years, and it is possible that additional, yet-undiscovered routes for functionalized ROOH that may be atmospherically relevant exist. In addition, several non-atmospheric sources such as those involved in autoignition in combustion engines, in the low-temperature interstellar medium, and in some catalytic reactions, have also been reported (Battin-Leclerc et al., 2010; Cox and Cole, 1985; Hu et al., 2023; Shan et al., 2017; Zhu et al., 2022), but they are not the focus of the present thesis.

The mechanistic diversity outlined above translates into a high frequency of hydroperoxide generation in the multigenerational VOC oxidation. As we have discussed in Chapter 1 and shown in Figure 4-2, GECKO-A simulations for representative VOCs (this would generate detailed chemical schemes according to prescribed reaction pathways), like *n*-octane and α -pinene, indicate that hydroperoxides constitute a substantial fraction of the tens of thousands of oxidation products generated. However, it is likely that GECKO-A modelling still misses explicit pathways such as those involving Criegee intermediates and higher-order autoxidation. As such, even these high predicted ROOH formation frequencies are likely conservative.

These functionalized molecules are of great atmospheric relevance in both the gas and particle phase. In the gas phase, hydroperoxides can participate in further oxidation or photolysis, releasing OH radicals and thereby acting as secondary radical sources (Jaeglé et al., 2000, 1997; Lee et al., 2000). Thermal or photochemical decomposition may also generate oxygen-centered radicals that initiate new reaction chains (Zhang et al., 2012). Their functional group properties, such as high polarity and moderate water solubility, make them efficient contributors to particle growth and SOA formation (Nguyen et al., 2015; Wang et al., 2023). In the condensed phase, hydroperoxides act as radical reservoirs and precursors, or as oxidants driving aqueous-phase transformation (Wang et al., 2023). A notable example is the oxidation of dissolved SO₂ to SO₄²⁻, leading to sulfate aerosol formation, which is a major component of PM_{2.5} associated with reduced air quality and visibility (Lind et al., 1987; Zhou and Lee, 1992). Furthermore, they can inhibit peroxidase enzymes crucial for plant defense and metabolic function (Hewitt et al., 1990; Marklund et al., 1971).

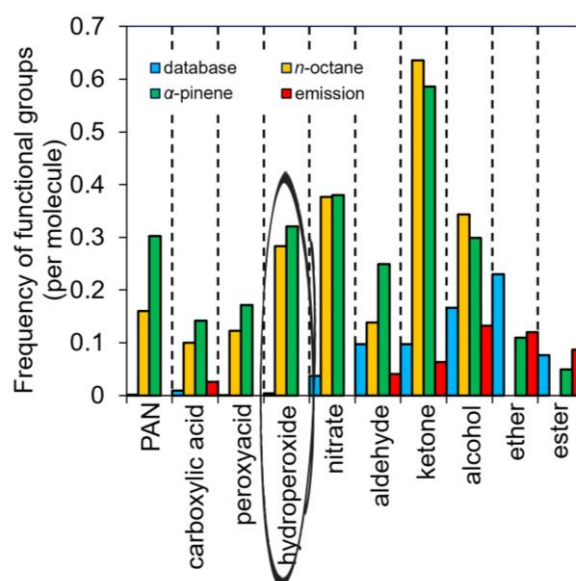


Figure 4-2. Frequency plots comparing the functionalization of compounds within the GECKO-A mechanism of *n*-octane and α -pinene oxidation; a database of anthropogenic emissions (Carter, 2015); and the compounds present in the kinetic database of (McGillen et al., 2020). The hydroperoxide group, emphasized here, is particularly underrepresented in the kinetic database. Data adapted from (McGillen et al., 2020).

Due to the undeniable importance of these oxidizing and functionalized hydroperoxides in atmospheric chemistry, there has been a great surge of interest in scientific community in exploring their underlying formation pathways and subsequent reaction mechanisms (Baker et al., 2024; Caravan et al., 2024; Dong et al., 2023; Harb et al., 2025; Illmann, 2025; Yang et al., 2025). Most atmospherically relevant ROOHs are multifunctional species, posing specific challenges to both experimental and theoretical characterization. Functional groups could change energetics or kinetics (e.g., barrier heights, exothermicities), potentially enabling new reaction channels and further molecular growth (Barber and Kroll, 2021). The reactivities of these molecules are not well-described by traditional structure-activity relationships (SARs), which require new experimental kinetic data (Vereecken et al., 2018). However, only a few alkyl hydroperoxides (e.g., methyl-, ethyl-, and tert-butyl hydroperoxides) are represented in current gas-phase kinetic databases and these are limited to OH oxidation (Carter, 2015; McGillen et al., 2020). The overall data scarcity of ROOHs stems primarily from their pronounced thermal instability, which poses significant explosion hazards during synthesis, isolation, and storage processes (Churchill, 2006; Wang and Shu, 2010). These safety constraints limit

the range of hydroperoxides that can be safely handled in laboratory environments, particularly because of the high-purity samples that are often required for kinetic experiments. Additional limitations arise from analytical challenges. Their instability makes them difficult to sample and separate using conventional gas chromatography techniques. In addition, their low volatility and reactivity make them prone to surface losses during measurement, which hinders their reliable introduction into kinetic systems, further complicating absolute rate coefficient determinations.

Accordingly, in this chapter, we employed a strategy of *in situ* “gas-phase synthesis” of hydroperoxides using a large-volume atmospheric simulation chamber. By conducting ethene ozonolysis in the presence of carboxylic acid, we selectively synthesized α -alkoxyacyl hydroperoxides with defined structures. Their gas-phase reactivities toward OH and NO₃ radicals, as well as Criegee intermediates, are subsequently characterized using the relative rate method in the chamber. In addition, tert-butyl hydroperoxide, one of the few commercially available ROOHs, was investigated for its reactivity with NO₃ radical and Criegee intermediate (CI), serving as a supplementary dataset and a benchmark for the ROOH measurements.

4.2 Experimental techniques

4.2.1 Chamber facilities

All experiments that are presented in this chapter were performed in the 90 m³ HELIOS atmospheric chamber at CNRS-ICARE (Orléans, France). General chamber facilities, instrumentation, mixing, pressure control, dilution tracking, and analytical platforms follow the same as those described previously. We therefore refer readers to Chapter 3, Section 3.2.1 and (Wang et al., 2025) for full specifications. In the present study, the actual experimental design and measurement details differ and are detailed in the following Section 4.2.2.

4.2.2 Relative rate experiments

Based on the chamber facilities described above, the experiments presented in this section were performed under dark conditions and followed a common sequence:

(i) *Background phase:*

We started each day with a clean chamber, which was achieved by prolonged zero-air flushing, at least overnight, plus chemical/physical clean-ups in a weekly manner. Before the first injection, we began monitoring with proton-transfer-reaction mass spectrometry (PTR-MS) and ensured that background masses indicative of residual chemistry from previous experiments fell below the instrument detection limits. The chamber was conditioned under overpressure with zero air, fans on, and SF₆ tracer-based dilution characterization. This background procedure follows our established protocol and will not be repeated in the following sections.

(ii) *Synthesis/injection phase:*

Next, target hydroperoxides were selectively generated through SCI insertion into a carboxylic acid in the gas phase, as illustrated in Figure 4-3. Alkene ozonolysis was used to generate available SCIs, and notably, this approach is not restricted to symmetric alkenes, and in contrast, using unsymmetrical alkenes allows the formation of multiple SCIs, thereby enabling the generation of diverse ROOH species. Carboxylic acid was used to scavenge SCIs generated to form α -alkoxyacyl hydroperoxides. Reactant ratios were chosen to favor insertion over competing channels, which was confirmed with the use of an explicit box model of the chamber conditions. The resulting hydroperoxides were monitored in real time using PTR-MS operated in NH₄⁺ mode, offering both sensitivity and selectivity toward these low-volatility, multifunctional compounds, whilst also minimizing ion fragmentation through low drift tube voltages.

In addition, we conducted measurements on *tert*-butyl hydroperoxide (TBHP), one of the only commercially accessible ROOHs, as a model compound to benchmark and complement our

observations. In this case, TBHP was introduced directly via a calibrated liquid injection through the injection manifold of the chamber.

Subsequent subsections follow this concept and provide more specific details.

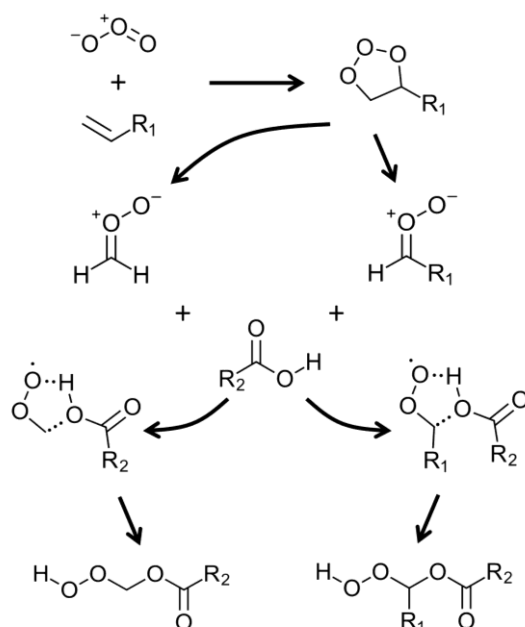


Figure 4-3. Generation mechanism of α -alkoxyacyl hydroperoxides via alkene ozonolysis in the presence of a carboxylic acid.

(iii) Stabilization phase:

In this phase, we were able to observe the stable time-series signals for individual compounds (including synthesized ROOHs), and we also added one or more reference compounds with known and well-defined kinetics. All the observable decays on the instrumental signals in this phase were dominated by non-chemical factors such as wall loss, dilution, and instrumental stability, and we therefore could conduct independent correction for individual compound to characterize extra physical losses.

(iv) Reactivity phase:

In this last phase, we triggered a single oxidation pathway (OH , NO_3 or SCI) by adding the oxidant precursors into the chamber. All the reactants were generated *in situ* and the first-order physical loss

for each compound was quantified independently as described above. Both the target compounds and reference compounds were lost solely via the selected oxidant (with no regeneration or interfering chemistry over the fitting phase), second-order rate coefficients were derived by the relative rate analysis relied on synchronized decays for the target ROOH and reference compounds:

$$\ln\left(\frac{[\text{compound}]_0}{[\text{compound}]_t}\right) - k_d t = \frac{k_{\text{compound}}}{k_{\text{reference}}} \ln\left(\frac{[\text{reference}]_0}{[\text{reference}]_t}\right) - k_d t \quad \text{Equation 4 - 1}$$

Here, $[\text{compound}]_0$ and $[\text{compound}]_t$ are the concentrations of the compound of interest at initial time and time t ; the same notation applies to the reference. The term k_d is the first-order, non-reactive loss for individual compounds. Linear regression of the corrected traces yields the slope $k_{\text{compound}}/k_{\text{reference}}$.

Operational details and considerations for oxidant use are provided in Table 4-1, Table 4-2, Table 4-3, and these subsections below.

4.2.2.1 Dark OH experiments

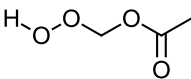
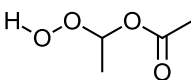
Following the experimental scheme described above, after the *background phase*, we started the *synthesis phase* by injecting an excess amount of ozone ($9.06\text{-}19.8 \times 10^{13}$ molecule cm^{-3}) and a controlled amount of acetic acid (1.74×10^{13} molecule cm^{-3}). A pulse of propene injection then initiated ozonolysis reactions, generating both formaldehyde oxide (CH_2OO) and *E/Z*-acetaldehyde oxide (*E/Z*- CH_3CHOO , the two conformers are not distinguished in this study). Both SCIs react rapidly with acetic acid to yield two ROOHs: hydroperoxymethyl acetate (HPMA) and hydroperoxyethyl acetate (HPEA), as illustrated in Figure 4-4.

Notably, [ozone] was maintained in excess to drive propene ozonolysis efficiently, while [acetic acid] input was limited. Acid loading had to be high enough to trap SCIs and favor ROOH formation, yet low enough to avoid significant OH scavenging in the subsequent *reactivity phase*. Propene loading was likewise balanced. Sufficient propene was required to generate detectable ROOH yields (via CH_2OO and CH_3CHOO insertion into acetic acid), but excessive propene leads to large amounts of carbonyl by-products (e.g., formaldehyde, acetaldehyde) that could act as strong OH scavengers and depress OH availability for the subsequent relative rate kinetics. Practically, we sought the minimum [acid] and

[propene] that produced reproducible ROOH signals while considering the OH availability, i.e., the projected pseudo-first order OH loss to acid and carbonyls remained small relative to that for target/reference. An explicit model simulation that estimates the ROOH yields and potential competing channels was found to be a useful and complementary approach for conducting these experiments, with modelling details to be presented in the following sections.

During the *stabilization phase*, cyclohexene oxide ($k_{\text{OH},298\text{ K}} = 6.21 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and 1-butene oxide ($k_{\text{OH},298\text{ K}} = 1.92 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were selected as reference compounds and injected into the chamber to be stabilized simultaneously with target ROOHs. Both have well-defined OH rate coefficients within a factor of five of the expected OH reactivity toward ROOH, and their concentrations were matched to the estimated [ROOH] (El Othmani et al., 2021a, 2021b). In addition to their suitable reactivity, both compounds were also chosen for their distinctive molecular masses that are not prone to spectral interference in this reactive system.

Table 4-1. Experimental conditions for the OH reactivity measurements of hydroperoxymethyl acetate and hydroperoxyethyl acetate reported in Table 4-4. All concentration data are in units of molecule cm^{-3} . Temperature is in units of Kelvin.

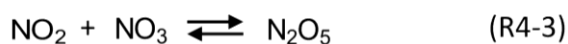
No	Compound	Synthesis			Stabilization	Reactivity	T
		[O ₃]	[propene]	[acetic acid]	[Reference]	[TME]	
OH-1	hydroperoxymethyl acetate	1.94×10 ¹⁴	4.81×10 ¹³	1.74×10 ¹³	4.54×10 ¹²	1.06×10 ¹⁴	294
OH-2		1.98×10 ¹⁴	4.91×10 ¹³	1.74×10 ¹³	4.54×10 ¹²	1.15×10 ¹⁴	297
OH-3		9.06×10 ¹³	4.44×10 ¹³	1.74×10 ¹³	4.54×10 ¹²	4.06×10 ¹³	291
OH-4	hydroperoxyethyl acetate	9.45×10 ¹³	4.52×10 ¹³	1.74×10 ¹³	4.54×10 ¹²	3.74×10 ¹³	294
OH-5		1.98×10 ¹⁴	4.91×10 ¹³	1.74×10 ¹³	4.54×10 ¹²	1.15×10 ¹⁴	297
OH-6		9.06×10 ¹³	4.44×10 ¹³	1.74×10 ¹³	4.54×10 ¹²	4.06×10 ¹³	291

Dark OH experiments were designed so that the target ROOHs and reference compounds were removed exclusively by OH radicals during the *reactivity phase*. Given the photolabile nature of hydroperoxides, common OH precursors such as methyl nitrite or H₂O₂, which rely on UV photolysis to produce OH, were avoided. As a robust alternative, OH radicals in the present study were generated

in the dark via ozonolysis of tetramethylethylene (TME, 2,3-dimethyl-2-butene). As a symmetric alkene, the reaction of TME with O₃ produces a single type of Criegee intermediates, acetone oxide. The dominant fate for both the excited and stabilized acetone oxide is expected to be isomerization to a vinyl hydroperoxide intermediate that undergoes O–O bond scission to yield OH radicals and a vinoxy-type radical, with a reported OH yield near unity ($\sim 93 \pm 14\%$) (IUPAC, 2025). TME was introduced into the chamber at a controlled flow rate under ozone-excess conditions to achieve observable decays of compounds of interest. Detailed concentration inputs for each compound are shown in Table 4-1.

4.2.2.2 NO₃ experiments

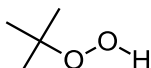
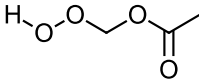
We determined NO₃ rate coefficients for ROOHs in two experimental sets. In the first set, TBHP was used as the target compound, with 2-propanol ($k_{\text{OH},298\text{ K}} = 1.40 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and butyraldehyde ($k_{\text{OH},298\text{ K}} = 1.10 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) selected as reference compounds (e.g., see Figure 4-7). In the *injection phase*, TBHP ($4.83 \times 10^{-12} \text{ molecule cm}^{-3}$) and a reference compound ($4.92\text{--}5.14 \times 10^{12} \text{ molecule cm}^{-3}$) were introduced directly into the chamber under an ozone background of $3.00 \times 10^{14} \text{ molecule cm}^{-3}$, followed by a *stabilization phase* of approximately one hour to account for first-order physical losses. In the *reactivity phase*, NO₃ radicals were generated by injecting NO ($7.49\text{--}14.3 \times 10^{11} \text{ molecule cm}^{-3}$) into the chamber in a controlled, pulse-wise manner. The specific reaction mechanism of NO₃ generation is as follows:



In the second set of experiments, HPMA and HPEA were *in situ* synthesized by propene ozonolysis in the presence of acetic acid (as in Section 2.2.2.1; see Figure 4-9). Because formaldehyde and acetaldehyde formed during propene ozonolysis are efficient NO₃ sinks that would potentially be competing with the intended ROOH oxidation, propene loading was then balanced to preserve NO₃ availability for the next *reactivity phase*. Detailed concentration inputs are listed in Table 4-2. 2-

butanol ($k_{\text{OH},298\text{ K}} = 2.00 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and acetaldehyde ($k_{\text{OH},298\text{ K}} = 2.70 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) were selected as the references, and the latter was inherently formed from propene ozonolysis and required no additional injection. NO_3 was then initiated with stepwise NO pulses under O_3 -excess conditions as described above.

Table 4-2. Experimental conditions for the NO_3 reactivity measurements of *tert*-butyl hydroperoxide and hydroperoxymethyl acetate reported in Table 4-6. All concentration data are in units of molecule cm^{-3} . Temperature is in units of Kelvin.

No	Compound	Injection + Stabilization			Reactivity		
		[compound]	$[\text{O}_3]$	[Reference]	[NO]	T	
NO_3 -1	<i>tert</i> -butyl hydroperoxide	4.83×10^{12}	3.00×10^{14}	4.92×10^{12}	1.43×10^{13}	297	
NO_3 -2		4.83×10^{12}	2.85×10^{14}	5.14×10^{12}	7.49×10^{12}	299	
No	Compound	Synthesis			Stabilization	Reactivity	
		[propene]	[acetic acid]	$[\text{O}_3]$	[Reference]	[NO]	T
NO_3 -3	hydroperoxymethyl acetate	4.47×10^{13}	1.74×10^{13}	2.96×10^{14}	–	4.39×10^{13}	299
		4.47×10^{13}	1.74×10^{13}	2.96×10^{14}	5.07×10^{12}	4.39×10^{13}	299

4.2.2.3 Criegee intermediate experiments

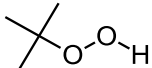
The bimolecular reaction kinetics of Criegee intermediate with ROOHs were also investigated based on the relative rate approach developed in Chapter 3 (ethene as a single SCI precursor, dark conditions, and OH suppression).

In the first set of experiments, TBHP was used as the target and was introduced into the chamber together with excess ozone and cyclohexane (e.g., Figure 4-11). A selection of alcohols (e.g., methanol, 2-propanol, and 2-butanol) was likewise introduced into the chamber during the injection phase, followed by the *stabilization phase* ~1h. In the reactivity phase, ethene was injected to initiate ozonolysis and generate CH_2OO as the oxidant. Detailed concentrations and reference information are

provided in Table 4-3, and detailed experimental protocols and methodology are provided in Chapter 3.

In the second set, HPMA and HPEA were *in situ* synthesized by propene ozonolysis in the presence of a carboxylic acid, following the strategy described in Sections 4.2.2.1 and 4.2.2.2. We found that in such a multi-ozonolysis system, the accumulated products complicate PTR-MS spectra, isovaleric acid was then selected as the acid precursor in order to shift the ROOH products to higher *m/z* and reduce spectral interference. Excess cyclohexane was used to suppress [OH]. Ethene ozonolysis was then conducted to produce CH₂OO as the oxidant in the *reactivity phase*. Detailed operational details and considerations are as described in Sections 4.2.2.1 and 4.2.2.2.

Table 4-3. Experimental conditions for the CI reactivity measurements of *tert*-butyl hydroperoxide and hydroperoxymethyl 3-methylbutanoate reported in Table 4-7. All concentration data are in units of molecule cm⁻³. Temperature is in units of Kelvin.

No	Compound	Injection + Stabilization				Reactivity	
		[compound]	[Reference]	[cyclohexane]	[O ₃]	[ethene]	T
CI-1	<i>tert</i> -butyl	4.83×10 ¹²	4.96×10 ¹²	3.17×10 ¹⁴	4.83×10 ¹⁴	8.00×10 ¹⁴	288
CI-2	hydroperoxide	4.83×10 ¹²	4.96×10 ¹²	3.17×10 ¹⁴	6.83×10 ¹⁴	1.22×10 ¹⁵	288
CI-3		4.83×10 ¹²	4.92×10 ¹²	3.17×10 ¹⁴	4.83×10 ¹⁴	8.00×10 ¹⁴	288
CI-4		4.83×10 ¹²	5.07×10 ¹²	3.17×10 ¹⁴	6.83×10 ¹⁴	1.22×10 ¹⁵	288

4.2.3 Chemicals

All chemicals used in this study were of analytical grade and employed without further purification. All the reagents used are listed here: ethene (≥99%, Linde), propene (≥99%, Air Liquide), *tert*-butyl hydroperoxide (≥70%, Sigma Aldrich), acetic acid (≥99%, TCI), valeric acid (≥98%, TCI), cyclohexane (≥99.5%, Sigma Aldrich), cyclohexene oxide (≥98%, Sigma Aldrich), 1-butene oxide (≥99%, TCI), methanol (≥99.8%, Sigma Aldrich), 2-propanol (≥99.95%, Fluka), 2-butanol (≥99.5%, Fluka). Zero air was generated using a custom-built purification system. Ozone was produced *in situ* using an ozone generator as described in Chapter 3, Section 3.2.2.

4.3 Results and discussion

4.3.1 OH oxidation

A representative time-series plot from a chamber-based relative rate experiment measuring the OH reactivity of the *in situ* synthesized α -alkoxyacyl hydroperoxides is shown in Figure 4-4, with the annotated labels indicating the successive experimental phases.

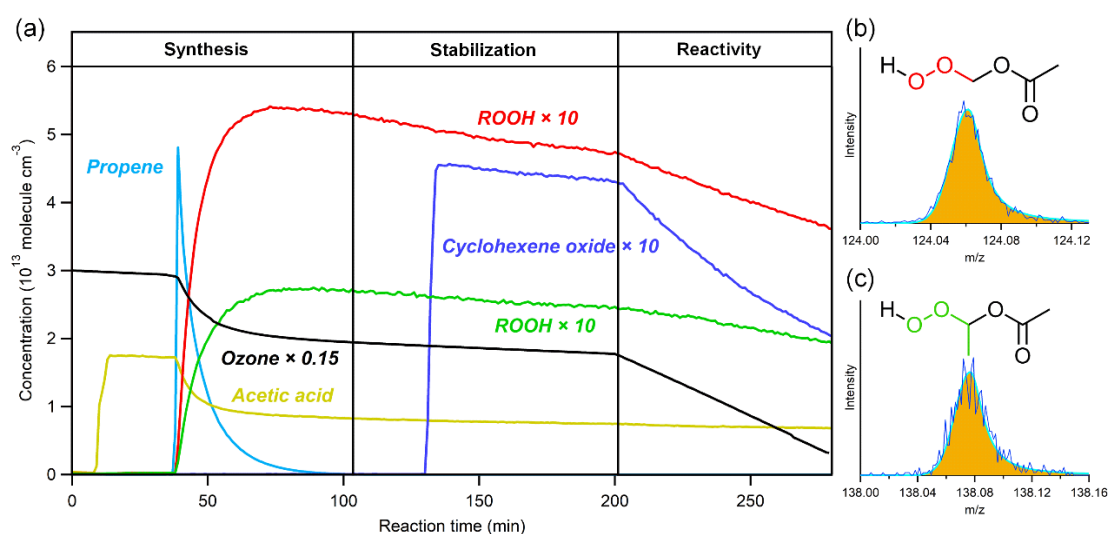


Figure 4-4. Panel (a) Time series of experimental data of an ozonolysis-synthesized α -alkoxyacyl hydroperoxide relative rate experiment, showing the *synthesis*, *stabilization* and *reactivity* phases. OH relative rate kinetics are obtained during the *reactivity phase* (see Figure 4-6), where OH radicals are generated via dark ozonolysis of tetramethylethylene. Mass spectra of the SCI insertion products into acetic acid (hydroperoxymethyl acetate and hydroperoxyethyl acetate) are shown in panels (b) and (c), respectively. Concentrations of both hydroperoxides are estimated through numerical simulation (see Table A4-1 for modelling details). Some experimental traces are multiplied by a scaling factor for clarity.

During the *synthesis phase*, propene injection initiated ozonolysis reactions, producing both CH_2OO and CH_3CHOO , and therefore leading to a concurrent decrease in ozone and acetic acid. Loss of acetic acid was dominated by its rapid insertion reactions with stabilized CH_2OO and CH_3CHOO , generating HPMA and HPEA respectively (Chhantyal-Pun et al., 2018; Wang et al., 2025). It is noted that no radical scavenger was added in these OH reactivity experiments, additional loss of acetic acid by other oxidants such as OH cannot be ruled out. Under O_3 -excess conditions, propene was completely

consumed within ~60 min, accompanied by the gradual formation of HPMA (red trace) and HPEA (green trace) as their monitored mass spectra shown in Figure 4-4 panel (b) and (c).

Concentrations of HPMA and HPEA were estimated using numerical simulations with details provided in Table A4-4. HPEA was observed at lower concentrations than HPMA, plausibly due to the combined factors including relative yields of CH_2OO and CH_3CHOO from propene ozonolysis, differences in their unimolecular decay rates, and possible stability differences between the two ROOHs. Nevertheless, this concentration difference is not expected to affect the kinetic measurement. In parallel, the corresponding dehydration products of HPMA and HPEA, namely anhydrides, were also observed to reach a steady level after formation as illustrated in Figure 4-5, consistent with observations described in Chapter 3. We attribute this prompt dehydration to the excess energy associated with ozonolysis reactions, where nascent SCIs insert into acids to yield ROOHs that retain sufficient internal energy to facilitate decomposition in the early stage of their formation (Behera et al., 2022).

During the *stabilization phase*, the radical budget in the system is expected to be very low, with no radical-initiation channels being operative during this phase. HPMA and HPEA exhibited gradual decays assumed to be physical losses (e.g., dilution and wall deposition), with cyclohexene oxide introduced as a reference compound to undergo the simultaneous loss for relative rate analysis. The *reactivity phase* was then initiated at ~200 min by a continuous flow of tetramethylethylene (TME), which was accompanied by a measurable decline in ozone. As a symmetric alkene, TME was ozonized by O_3 to generate one type of Criegee intermediate, acetone oxide, which produced OH radicals in a high yield as described above. Although acetone oxide could, in principle, also act as an oxidant toward ROOHs or reference, its contributions were expected to be negligible compared to OH reactions under our experimental conditions, especially given the presence of residual acetic acid and abundant carbonyl by-products (e.g., formaldehyde, acetaldehyde) that efficiently outcompete such pathways.

Through careful regulation of TME input, we obtained analyzable decays of HPMA, HPEA and the reference compound, allowing Equation 4-1 to be applied to derive the relative rate plots. All the relative rate plots for OH reactivity of HPMA and HPEA are shown in Figure 4-5, exhibiting satisfactory linearity and low scatter.

It should be noted that, in these experiments, sequential ozonolysis reactions in the chamber generated a large number of reaction products that significantly contribute additional m/z peaks in the PTR-MS spectra. This has led to spectral interference for many reference compounds in our preliminary experiments. Interestingly, the two chosen epoxides (cyclohexene oxide and 1-butene oxide) were excluded from such interference under our conditions, suggesting that these molecular structures and their isomers are not readily produced in ozonolysis systems.

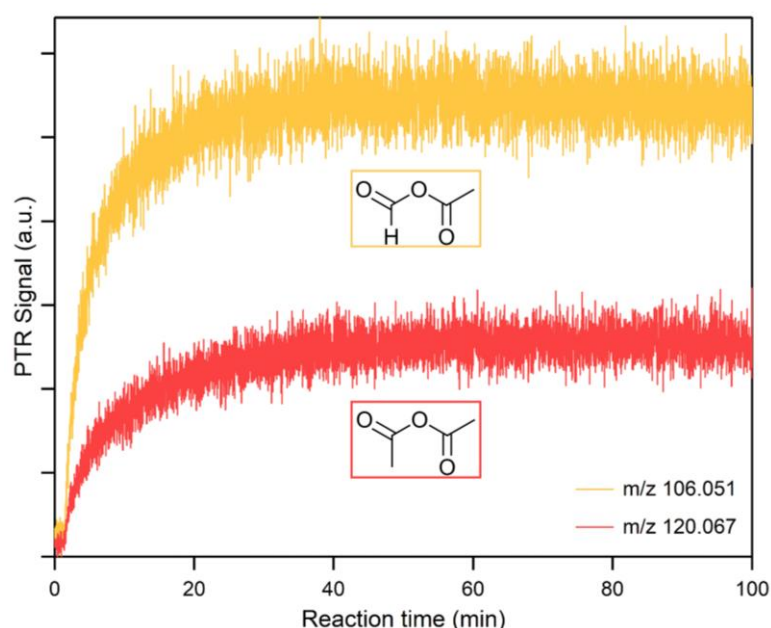
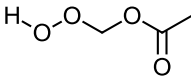
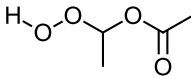


Figure 4-5. Temporal PTR-MS traces of the selected m/z signals corresponding to acetic formic anhydride (m/z 106.051, yellow trace) and ethanoic anhydride (m/z 120.067, red trace) from experiments shown in Figure 4-4.

Tabulated OH relative rate coefficients and associated analysis parameters are presented in Table 4-4. Excellent consistency and reproducibility were observed across different experiments, indicating that secondary radical chemistry /heterogeneous processes, or other potential interferences are not a major concern under these conditions. Based on error-weighted averaging of multiple determinations, we give the recommended rate coefficients at room temperature of $(1.65 \pm 0.10) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for HPMA and $(2.01 \pm 0.13) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for HPEA. Reported uncertainties include both the regression error of the derived slopes (2σ) and the estimated uncertainties of the reference rate coefficients (taken from the Database for the Kinetics of the Gas-Phase Atmospheric Reactions of Organic Compounds v2.1.0 (McGillen et al., 2020), available at

<https://data.eurochamp.org/data-access/kin/#/home>). Detailed error analysis procedure follows the same as described in Chapter 3, Section 3.2.4.

Table 4-4. Tabulated OH rate coefficients for the hydroperoxymethyl acetate and hydroperoxyethyl acetate, together with analysis parameters. The detailed measurement conditions corresponding to this table can be found in Table 4-1.

No	Target compound	<i>k</i> compound ^a	Method ^b	Reference compound	<i>k</i> reference ^c	Slope ^d
OH-1	hydroperoxymethyl acetate	$(1.64 \pm 0.25) \times 10^{-12}$	RR	cyclohexene oxide	$(6.18 \pm 0.93) \times 10^{-12}$	0.266 ± 0.006
OH-2	(HPMA)	$(1.61 \pm 0.24) \times 10^{-12}$	RR	cyclohexene oxide	$(6.09 \pm 0.91) \times 10^{-12}$	0.264 ± 0.005
OH-3		$(1.64 \pm 0.25) \times 10^{-12}$	RR	cyclohexene oxide	$(6.24 \pm 0.94) \times 10^{-12}$	0.263 ± 0.004
OH-4		$(1.66 \pm 0.25) \times 10^{-12}$	RR	cyclohexene oxide	$(6.18 \pm 0.93) \times 10^{-12}$	0.268 ± 0.003
OH-5		$(1.67 \pm 0.26) \times 10^{-12}$	RR	1-butene oxide	$(1.86 \pm 0.28) \times 10^{-12}$	0.900 ± 0.029
OH-6		$(1.67 \pm 0.26) \times 10^{-12}$	RR	1-butene oxide	$(1.86 \pm 0.28) \times 10^{-12}$	0.900 ± 0.029
		$(1.65 \pm 0.10) \times 10^{-12}$	<i>recommended</i> ^e			
OH-1	hydroperoxyethyl acetate	$(2.03 \pm 0.31) \times 10^{-12}$	RR	cyclohexene oxide	$(6.18 \pm 0.93) \times 10^{-12}$	0.329 ± 0.008
OH-2	(HPEA)	$(1.94 \pm 0.30) \times 10^{-12}$	RR	cyclohexene oxide	$(6.09 \pm 0.91) \times 10^{-12}$	0.319 ± 0.009
OH-3		$(2.01 \pm 0.31) \times 10^{-12}$	RR	cyclohexene oxide	$(6.24 \pm 0.94) \times 10^{-12}$	0.322 ± 0.010
OH-4		$(2.01 \pm 0.30) \times 10^{-12}$	RR	cyclohexene oxide	$(6.18 \pm 0.93) \times 10^{-12}$	0.325 ± 0.004
OH-5		$(2.02 \pm 0.32) \times 10^{-12}$	RR	1-butene oxide	$(1.86 \pm 0.28) \times 10^{-12}$	1.085 ± 0.053
OH-6		$(2.05 \pm 0.32) \times 10^{-12}$	RR	1-butene oxide	$(1.86 \pm 0.28) \times 10^{-12}$	1.104 ± 0.038
		$(2.01 \pm 0.13) \times 10^{-12}$	<i>recommended</i> ^e			

^aUnits of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, errors are reported at weighted averages of reference rate constants and measured slopes.

^b"RR" = relative rate. ^cUnits of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, reference rate coefficients referred from (McGillen et al., 2020) with error

estimated in this database. ^dMeasured slopes, errors are 2σ . ^eRecommended values are error-weighted means, where

multiple measurements are available.

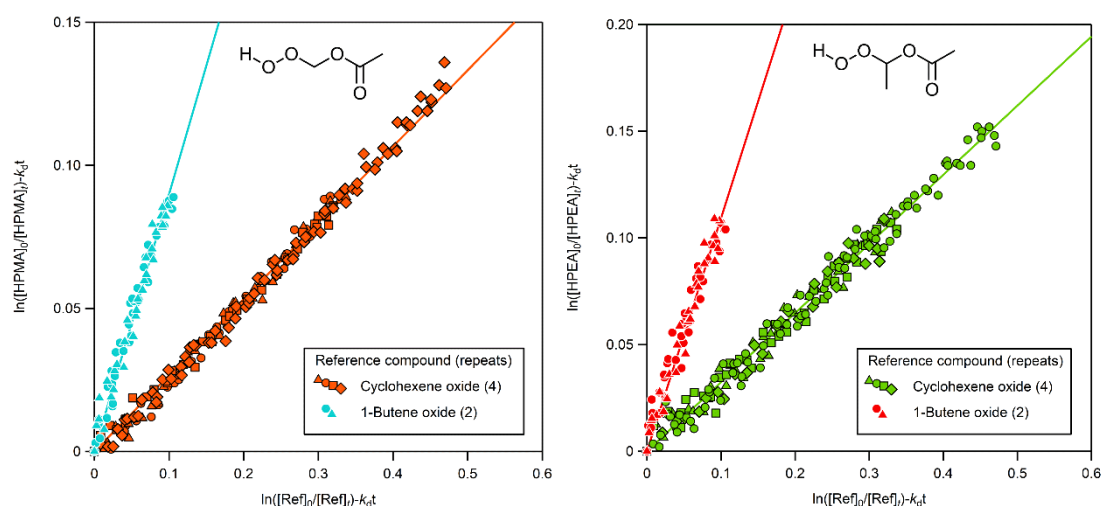


Figure 4-6. Relative rate plots used to derive OH kinetics for ozonolysis-synthesized α -alkoxyacyl hydroperoxide. *Left* panel shows the relative rate data for hydroperoxymethyl acetate, while *right* panel corresponds to hydroperoxyethyl acetate. Kinetics are obtained during the *reactivity phase* of the experiments (e.g., see Figure 4-4), using cyclohexene oxide and 1-butene oxide as reference compounds. Different symbols are used to distinguish separate experiments, demonstrating the precise reproducibility of these data.

Prior gas-phase kinetics for organic hydroperoxides are sparse and, where available, are almost exclusively limited to the measurements with OH radicals (Carter, 2015; IUPAC, 2025; McGillen et al., 2020). Here we summarized the available measurements and associated parameters in Table 4-5. Reported rate coefficients for simple hydroperoxides containing one “–OOH” group generally fall within the 10^{-11} – 10^{-12} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ range. However, significant discrepancies exist, for instance, the reported values of methyl hydroperoxide derived from relative and absolute rate methods differ by nearly a factor of two, a divergence explicitly noted by (IUPAC, 2025). For ethyl hydroperoxide, the only reported study was likely affected by photolysis corrections and potential $\text{RO}_2 + \text{HO}_2$ back-reactions regenerating the parent ROOH, and the IUPAC evaluation has therefore reinterpreted the result as a lower limit (IUPAC, 2025). In contrast, the implementation of dark OH generation via TME ozonolysis under our experimental conditions avoids the need for additional corrections associated with photolysis processes, and also ensure a relatively low HO_2 budget in the system, thereby suppressing the potential regeneration of parent ROOH species through $\text{RO}_2 + \text{HO}_2$ reactions, which would otherwise interfere with the kinetic determination. To further evaluate this, a near-explicit

zero-dimensional box model containing ~250 chemical reactions was constructed to reproduce the experimental conditions (see Figure 4-7).

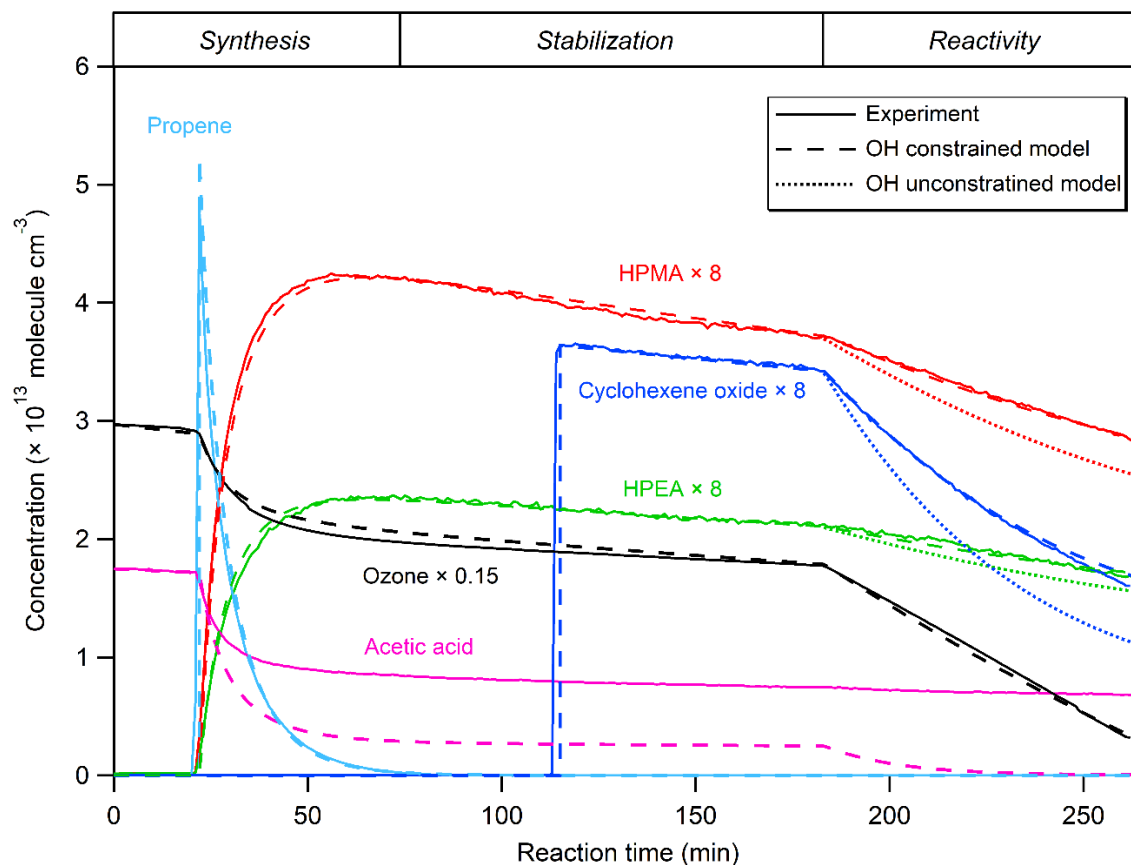


Figure 4-7. Updated time-series of a representative ozonolysis-synthesized α -alkoxyacyl hydroperoxide relative rate experiment, showing the experimental data (solid, same as Figure 4-4) and associated chemical box model outputs (dashed and dotted).

The model successfully reproduces the observed temporal profiles during the synthesis and stabilization phases. Propene and ozone decays are well captured, leading to satisfactory agreement for the formation and evolution of the two ROOH species. The experimental ROOH concentrations were scaled to match the absolute levels predicted by the model simulation. A notable deviation is observed for acetic acid. This discrepancy is attributed to mass interference from an isomeric species contributing to the same PTR-MS signal (m/z 78, $\text{CH}_3\text{C}(\text{O})\text{OHNH}_4^+$), originating from ongoing chamber chemistry, which is not fully resolved in the model framework.

However, significant discrepancies emerge during the reactivity phase when simulating the OH budget (dotted lines in Figure 4-7). The initial model configuration systematically overestimates the decay rates of the target ROOH species relative to experimental observations, indicating an overprediction of OH concentrations. This discrepancy likely arises from combined limitations in both OH sources and sinks. First, even with ~250 reactions included, it is impractical to incorporate every minor reaction pathway required to fully constrain the OH budget. Accumulated oxidation products and secondary intermediates can contribute additional OH sinks that are not comprehensively represented in the mechanism. Second, in this system, OH is produced through the unimolecular decomposition of both excited and stabilized Criegee intermediates via β -hydrogen abstraction forming a vinyl hydroperoxide intermediate. The first-order decomposition rate constant of vinyl hydroperoxide to yield OH remains highly uncertain. In the present model, we adopt the theoretical rate coefficient reported by Guo et al. (2017), $k = 0.68 \text{ s}^{-1}$ at room temperature. However, experimental evidence suggests a characteristic timescale of approximately 100 ms for this process (Drozd et al., 2011), corresponding to a rate constant nearly seven times larger. Such discrepancies introduce substantial uncertainty in the modeled OH source strength.

Together, these uncertainties on both the source and sink sides complicate accurate representation of the OH budget in the experiment. To reconcile model predictions with experimental observations, an additional loss pathway for vinyl hydroperoxide was introduced in the constrained model configuration. A comparison of the simulated total OH reactivity in the constrained and unconstrained models is shown in Figure 4-8. By comparison to the constrained model, the unconstrained model accounts for 62% OH reactivity at the beginning of the *reactivity* phase and 60% OH reactivity at the end of the experiment. These ~40% missing OH reactivities may arise from either the uncertainty in either the absolute value of the decomposition rate of vinyl hydroperoxide or accumulated other by-products in the secondary chemistry. Nevertheless, this empirical adjustment effectively moderates OH production and enables satisfactory reproduction of the observed decay profiles (dashed lines in Figure 4-7), resulting in a more realistic HO_x budget.

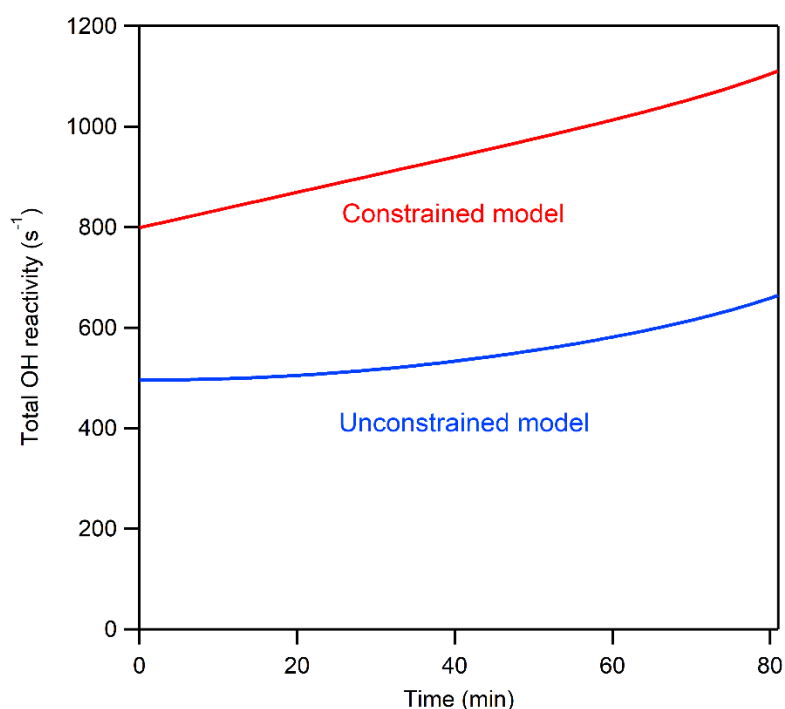


Figure 4-8. Comparison of total OH reactivities (s^{-1}) in the constrained (red) and unconstrained (blue) models for the *reactivity* phase shown in Figure 4-7.

Importantly, application of a tagged model during the *reactivity* phase enables quantitative attribution of the ROOH loss pathways. The results demonstrate that the decay of both ROOH species is overwhelmingly dominated by reaction with OH. Throughout the *reactivity* phase of the experiment, OH accounts for 99.95–99.57% of HPMA loss and 99.97–99.44% of HPEA loss. Oxidation by acetone oxide represents the second most important pathway, yet its contribution still remains below 1%. All other channels, including reactions with HO_2 , RO_2 , and RO radicals, are negligible, contributing less than 0.01% to the overall ROOH loss.

In addition to direct loss processes, potential regeneration of ROOH via $\text{RO}_2 + \text{HO}_2$ reactions was evaluated within the constrained model. The calculated regeneration fractions amount to only 2.08% for HPMA and 1.96% for HPEA at the end of the experiment. These results confirm that secondary reformation pathways are minor relative to the dominant OH sink and do not introduce significant bias into the kinetic determination.

Table 4-5. Tabulated rate coefficients for hydroperoxides from previous studies, together with the experimental conditions and primary apparatus.

Target compound	Oxidant	k^a	Method ^b	Measurement ^c	T ^d	P ^e	Source
Hydroperoxymethyl hydroperoxide	OH	$(7.1 \pm 1.5) \times 10^{-12}$	RR	CIMS	295	745	(Allen et al., 2018)
Methyl hydroperoxide	OH	5.54×10^{-12}	Abs	PLP-LIF	298	100-400	(Vaghjiani and Ravishankara, 1989)
	OH	$(1.02 \pm 0.08) \times 10^{-11}$	RR	FTIR	~298	700	(Niki et al., 1983)
Ethyl hydroperoxide	OH	$(5.92 \pm 0.36) \times 10^{-12}$	RR	FTIR	293 ± 2	760	(Wang and Chen, 2008)
<i>t</i> -butyl hydroperoxide	OH	$(3.58 \pm 0.54) \times 10^{-12}$	Abs	PLP-LIF and FTIR	296	90-200	(Baasandorj et al., 2010)
	CH ₂ OO	$(1.2^{+1.2}_{-0.6}) \times 10^{-13}$	Abs	MPI-MS	300	10	(Caravan et al., 2024)

^aUnits of cm³ molecule⁻¹ s⁻¹, errors are reported by the original papers. ^bMethod abbreviations: “RR” = relative rate, “abs” = absolute method. ^cMeasurement abbreviations: “CIMS” = chemical ion mass spectrometry, “PLP-LIF” = pulsed laser photolysis-laser induced fluorescence, “FTIR” = Fourier-transform infrared spectroscopy, “MPI-MS” = multiphoton-ionization mass spectrometry. ^dUnits of Kelvin. ^eUnits of Torr.

Hydroxymethyl hydroperoxide, an insertion product of CH₂OO + H₂O and abundant in the atmosphere, appears to exhibit OH reactivity comparable to, or slightly faster than, that of methyl-, ethyl-, or *tert*-butyl hydroperoxide. Against this backdrop, the OH rate coefficients of HPMA and HPEA determined in this work are distinctly lower than these of reported hydroperoxides. For *tert*-butyl hydroperoxide, which lacks α -hydrogen atoms being the reactive sites, OH abstraction is expected to occur predominantly at the –OOH site. The addition of α -hydrogen atoms, as in methyl- and ethyl-hydroperoxide, does not appear to significantly enhance the overall reactivity, suggesting that the methyl substituent acts mainly as an electron-donating group with only a modest impact on the reaction rate. By comparison, the α -alkoxyacyl substitution in HPMA and HPEA introduces an electron-withdrawing effect, which we hypothesize that this may reduce the reactivity at the –OOH site. This interpretation is further supported by bond dissociation energy (BDE) calculation (John et al., 2020), where the BDE of the O–H bond at the –OOH site in TBHP is estimated to be 81.6 kcal mol⁻¹ but in

HPMA it rises to 89.6 kcal mol⁻¹. Such can be a big difference reflected in the reactivity. This electronic impact could plausibly account for the lower OH rate coefficients observed for these α -alkoxyacyl hydroperoxides. Nevertheless, a broader mechanistic understanding of how additional oxygenated substituents modulate the intrinsic reactivity of ROOH remains an open question and warrants further investigation.

4.3.2 NO₃ oxidation

The gas-phase reactivity of organic hydroperoxides with NO₃ radicals remains essentially unknown (McGillen et al., 2020), even for simple compounds containing only a single –OOH group. We therefore investigated the reaction of NO₃ with TBHP as a first benchmark. A representative time-series plot of a relative rate experiment measuring NO₃ reactivity of TBHP is shown in Figure 4-9. In this experiment, excess ozone, TBHP (purple trace) and the reference compound (here butyraldehyde, green trace) were introduced during the *injection phase*, followed by a ~100 min *stabilization phase*. Upon pulsed NO injection, NO rapidly reacted with O₃ to form NO₂, which in turn reacted with O₃ to generate NO₃ radicals, triggering the concurrent decays of TBHP and butyraldehyde. The inflection in both traces at ~170 min marked the second NO injection. Each NO pulse also resulted in the expected consumption of O₃.

Applying model simulations to the *reactivity phase* provided quantitative estimates of secondary products, such as peroxyacyl nitrate (*n*-C₃H₇C(O)O₂NO₂, PAN) shown in Figure 4-9. This PAN is primarily generated through hydrogen abstraction of butyraldehyde by NO₃, yielding *n*-C₃H₇C(O)O₂ radicals that subsequently combine with NO₂. For TBHP, lacking α -H, abstraction is expected at the –OOH hydrogen, yielding (CH₃)₃CO₂ radicals. (CH₃)₃CO₂ can react with NO₂ to form the corresponding peroxyxynitrate as (CH₃)₃CO₂NO₂, and we indeed observed signals attributable to this species, primarily as fragments such as *m/z* 64.027 (NO₂NH₄⁺) that likely due to its intrinsic instability under the current voltage and temperature settings in the drift tube of PTRMS. Modelling details can be found in Table A4-1.

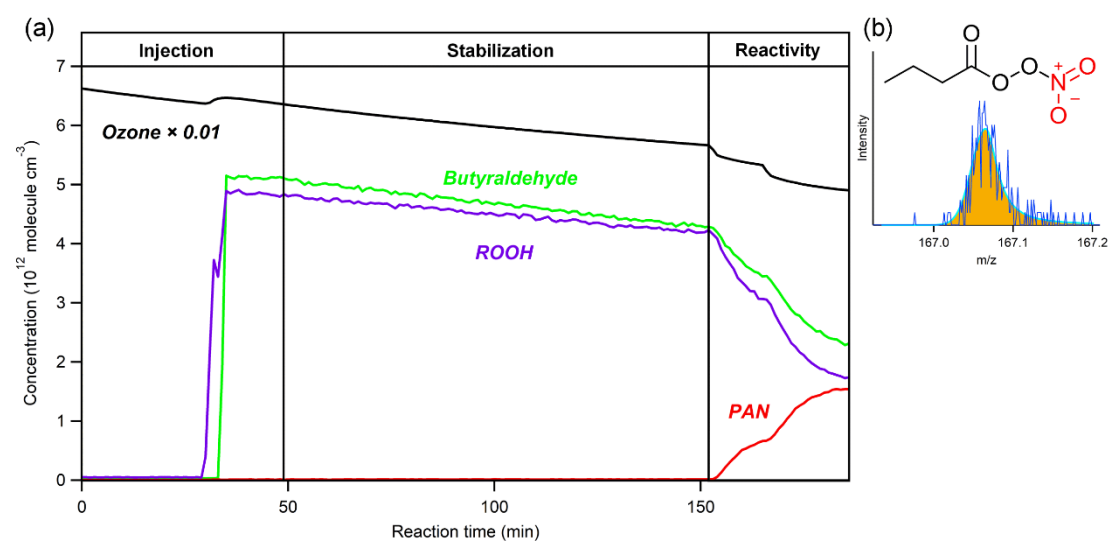


Figure 4-9. Panel (a) Time series of experimental data of a *tert*-butyl hydroperoxide relative rate experiment, showing the *injection*, *stabilization* and *reactivity* phases. NO_3 relative rate kinetics are obtained during the *reactivity* phase (see Figure 4-10), where NO_3 radicals are generated via NO injections in the presence of ozone. The peak associated with peroxyacyl nitrate (peroxy-*n*-butryl nitrate), whose concentration is estimated through numerical simulation, is shown in panel (b). Ozone is scaled by a factor of 0.01 for better visualization.

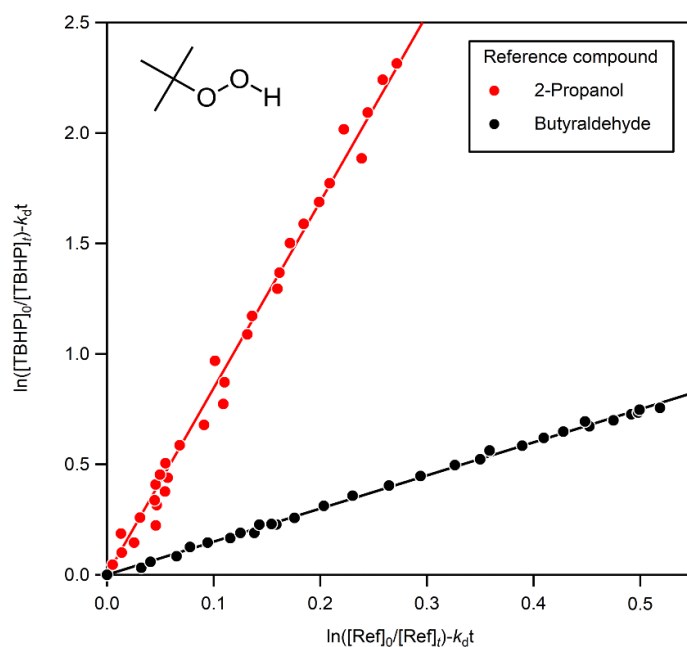


Figure 4-10. Relative rate plot used to derive NO_3 kinetics for *tert*-butyl hydroperoxide. Kinetics are obtained during the *reactivity* phase of the experiments (e.g., see Figure 4-9), using 2-propanol and butyraldehyde as reference compounds.

The relative rate plots for TBHP oxidation by NO₃, obtained with 2-propanol and butyraldehyde as references, are displayed in Figure 4-10, exhibiting excellent linearity in both cases. The tabulated results are provided in Table 4-6, giving a recommended rate coefficient at room temperature of $(1.58 \pm 0.22) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the TBHP + NO₃ reaction.

In a separate set of experiments, HPMA and HPEA were generated via propene ozonolysis in the presence of acetic acid, and their reactivity toward NO₃ was then determined. A time-series plot is shown in Figure 4-11.

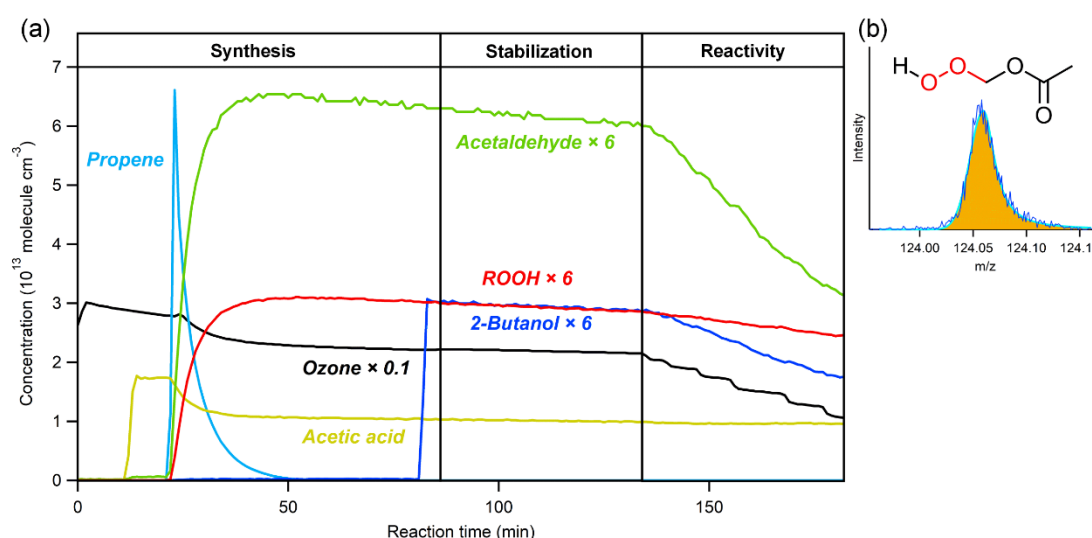


Figure 4-11. Panel (a) Time series of experimental data of an ozonolysis-synthesized α -alkoxyacyl hydroperoxide relative rate experiment, showing the *synthesis*, *stabilization* and *reactivity* phases. NO₃ relative rate kinetics are obtained during the *reactivity phase* (see Figure 4-12), where NO₃ radicals are generated via NO injections in the presence of ozone. Mass spectrum of the SCI insertion products into acetic acid is shown in panel (b). Concentration of resulting hydroperoxide is estimated through numerical simulation (see Table A4-1 for modelling details). Some experimental traces are multiplied by a scaling factor for clarity.

During the *synthesis phase*, propene and excess O₃ were introduced, the resulting CH₂OO and CH₃CHOO inserted into acetic acid to form HPMA and HPEA. Propene was essentially consumed at ~50 min as the HPMA signal (red trace) increased and then stabilized in the subsequent *stabilization phase*, and O₃ and acetic acid decreased slowly at the same time. The concentrations of HPMA in this

experiment were estimated by running a box model as detailed in Table A4-1. Acetaldehyde (produced from propene ozonolysis) and 2-butanol (added by liquid injection) served as reference compounds. In the *reactivity phase*, NO was added in the excess O₃ background. NO was rapidly converted to NO₂ and then to NO₃, driving synchronous decays of HPMA and the references. Each NO pulse was accompanied by a measurable O₃ decrease, consistent with the NO→NO₂→NO₃ conversion.

It should be noted that HPEA is not presented in Figure 4-11. Propene ozonolysis inevitably generates a suite of carbonyl by-products, and some of them, such as acetaldehyde, react effectively with NO₃ and were used here as a reference compound. Under these conditions, the lower concentration of HPEA with these competing channels existing kept the fractional loss of HPEA toward NO₃ below the detection threshold of our analysis. Therefore, we only report kinetics for HPMA here.

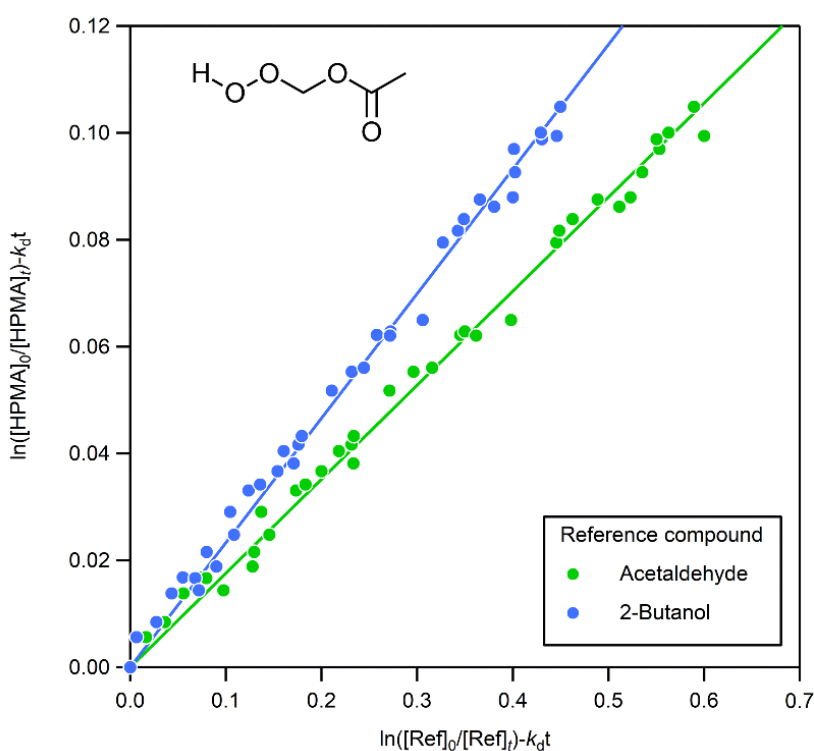
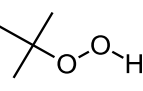
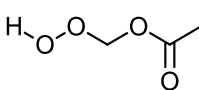


Figure 4-12. Relative rate plot used to derive NO₃ kinetics for ozonolysis-synthesized hydroperoxymethyl acetate. Kinetics are obtained during the *reactivity phase* of the experiments (e.g., see Figure 4-11), using acetaldehyde and 2-butanol as reference compounds.

Regarding concerns over other radical chemistry, HO_x radicals were not expected to interfere measurably with the NO₃ kinetics during the *reactivity phase*. NO was quickly consumed by O₃, a substantial level of NO₂ was maintained, and NO₃ in the chamber was continuously produced from NO₂ + O₃ or in equilibrium with N₂O₅ while residual NO remained low. Under these conditions, any RO₂ formed in the mixture would preferentially combine with NO₂ to give RO₂NO₂, and even if RO₂ self- or cross-reactions produced RO that reacted with O₂ to form a carbonyl and HO₂, the HO₂ was captured by NO₂ as HO₂NO₂. Although HO₂NO₂ can thermally decompose back to HO₂ and NO₂, this cycling lowers the effective radical budget. The reaction of HO₂ + NO₃ → OH + NO₂ + O₂ was therefore not competitive, and any OH formed would be rapidly sequestered by NO_x, for example by reaction with NO₂ to form HNO₃ or with NO to HONO. Consistent with these thoughts, the HPMA relative rate plots using acetaldehyde and 2-butanol as references show good linearity and zero intercepts (Figure 4-12). Tabulated NO₃ rate coefficients for HPMA are provided in Table 4-6, where we put the recommended value of $(4.81 \pm 0.80) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for HPMA + NO₃.

According to Table 4-6, the NO₃ reactivity of HPMA is found to be substantially lower than that of TBHP, by a factor of ~33. This reactivity reduction is consistent with our OH measurements, where the OH rate coefficient of HPMA determined in this study is nearly a factor of two smaller than the previously reported value for TBHP by (Baasandorj et al., 2010). These observations suggest that the reaction mechanisms of OH and NO₃ with hydroperoxide may share similarities, with hydrogen abstraction likely occurring at the –OOH site. However, the α-alkoxyacyl substitution has a much stronger damping effect on NO₃ reactivity than on OH reactivity, implying that the local electronic environment around –OOH may influence NO₃-mediated H-abstraction more severely. At present, with machine learning techniques based on large quantum chemical datasets, the BDE calculations provide an accessible way to indicate the electron-withdrawing effect from the OOH system due to α-alkoxyacyl substitution (John et al., 2020). Nevertheless, there is a lack of quantum chemical investigations into such systems, and targeted computational studies would be essential to assess how oxygenated substituents modulate the energetics of H-abstraction by NO₃.

Table 4-6. Tabulated NO₃ rate coefficients for the *tert*-butyl hydroperoxide and hydroperoxymethyl acetate, together with analysis parameters. The detailed measurement conditions corresponding to this table can be found in Table 4-2.

No	Target compound	<i>k</i> ^a	Method ^b	Reference compound	<i>k</i> ref ^c	Slope ^d
NO ₃ -1	<i>tert</i> -butyl hydroperoxide	(1.18±0.47)×10 ⁻¹⁴	RR	2-propanol	(1.40±0.56)×10 ⁻¹⁵	8.451±0.180
NO ₃ -2	(TBHP) 	(1.70±0.26)×10 ⁻¹⁴	RR	butyraldehyde	(1.13±0.17)×10 ⁻¹⁴	1.499±0.013
		(1.58±0.22)×10 ⁻¹⁴	<i>recommended</i> ^e			
NO ₃ -3	hydroperoxymethyl acetate (HPMA) 	(4.89±0.98)×10 ⁻¹⁶	RR	acetaldehyde	(2.78±0.56)×10 ⁻¹⁵	0.176±0.003
		(4.66±1.60)×10 ⁻¹⁶	RR	2-butanol	(2.00±0.60)×10 ⁻¹⁵	0.233±0.004
		(4.81±0.80)×10 ⁻¹⁶	<i>recommended</i> ^e			

^aUnits of cm³ molecule⁻¹ s⁻¹, errors are reported at weighted averages of reference rate constants and measured slopes.

^b“RR” = relative rate. ^cUnits of cm³ molecule⁻¹ s⁻¹, reference rate coefficients referred from (McGillen et al., 2020) with error estimated in this database. ^dMeasured slopes, errors are 2σ. ^eRecommended values are error-weighted means, where multiple measurements are available.

4.3.3 Criegee intermediate oxidation

Criegee intermediate reactivity toward organic hydroperoxide was characterized in this section, with *tert*-butyl hydroperoxide chosen as the initial benchmark using the chamber-based relative rate methodology established in Chapter 3. Figure 4-13 illustrates a representative time series of the relative rate experiments measuring CI reactivity of TBHP.

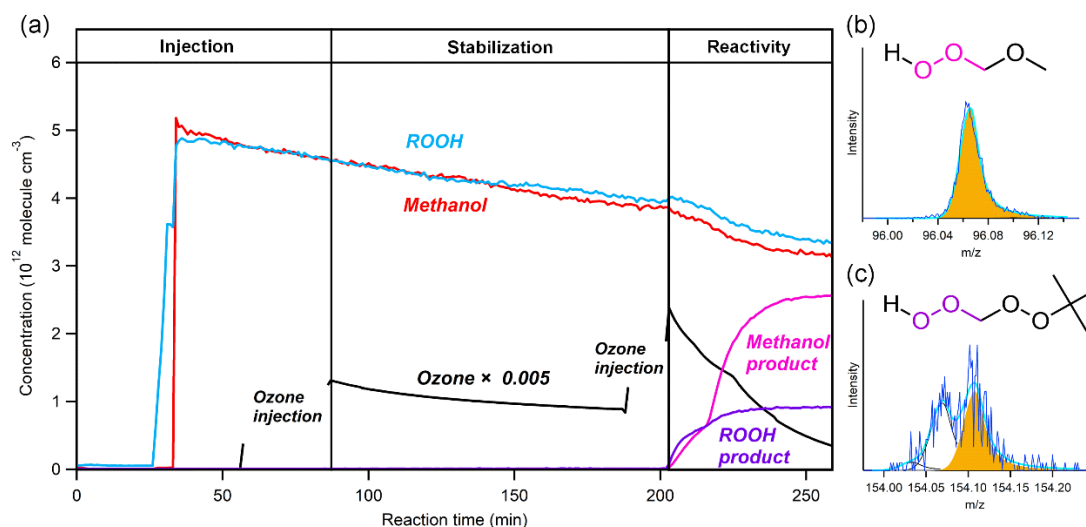


Figure 4-13. Panel (a) Time series of experimental data of a tert-butyl hydroperoxide relative rate experiment, showing the *injection*, *stabilization* and *reactivity* phases. SCI relative rate kinetics are obtained during the *reactivity* phase (see Figure 4-14), where SCIs are generated via ethene ozonolysis. Mass spectra of the SCI insertion products into methanol and tert-butyl hydroperoxide (hydroperoxymethyl ether and hydroperoxymethyl tert-butyl peroxide) are shown in panels (b) and (c), respectively. Concentration of both insertion products are estimated through numerical simulation (see Table A4-4 for modelling details). Ozone is scaled by a factor of 0.005 for better visualization, with some data points missing during the ozone injection due to measurement noise.

During the *injection* phase, TBHP (blue trace) and methanol (red trace, as the reference compound) were added into the chamber, along with excess ozone, and cyclohexane as an OH scavenger. After a *stabilization* phase of ~ 120 min, ethene was injected and reacted with O_3 to produce CH_2OO , which acted as the oxidant and initiated insertion reactions that led to the concurrent decay of TBHP and methanol. Product signals were detected for CH_2OO insertion into the O–H bonds of both methanol and TBHP (Figure 4-13, panel b and c). Insertion into methanol yields an α -alkoxyalkyl hydroperoxide ($\text{CH}_3\text{OCH}_2\text{OOH}$), while insertion at the –OOH site in TBHP leads to a highly oxygenated product ($(\text{CH}_3)_3\text{COOCH}_2\text{OOH}$). Concentrations of these products were explicitly modelled using a box model simulation, with details provided in Table A4-4.

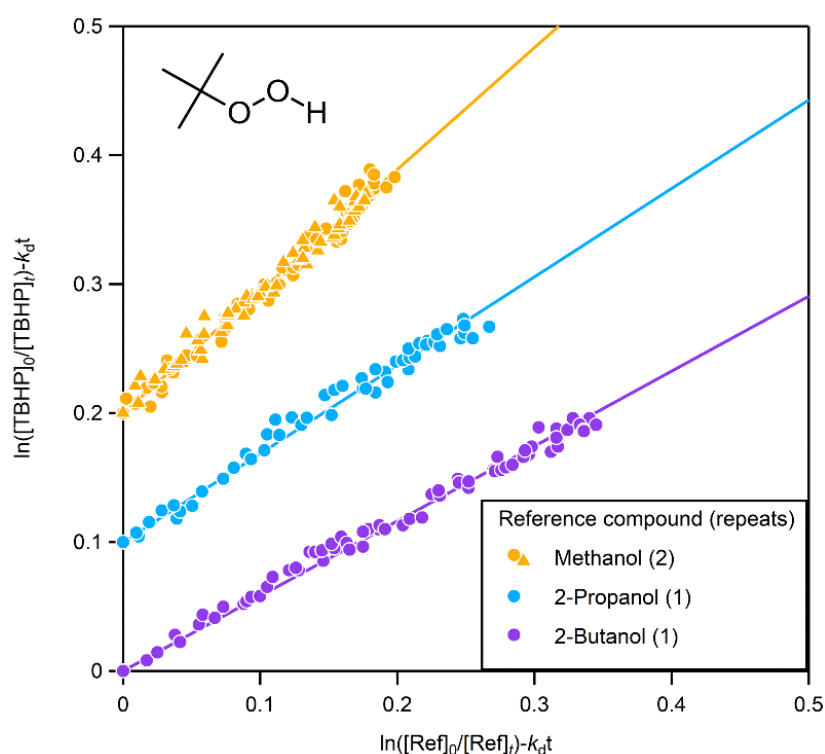
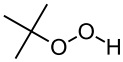


Figure 4-14. Relative rate plot used to derive SCI kinetics for *tert*-butyl hydroperoxide. Kinetics are obtained during the *reactivity phase* of the experiments (e.g., see Figure 4-13), using methanol, 2-propanol and 2-butanol as reference compounds. For clarity, relative rate traces are offset by 0.2 (for methanol as the reference) and 0.1 (for 2-propanol as the reference) in the y-axis.

Because the reactivity of TBHP with CH_2OO appeared to be comparable to that of alcohols, alcohols characterized in Chapter 3 can be used as reference compounds. Relative rate analysis with methanol, 2-propanol, and 2-butanol are presented in Figure 4-14, again, showing good linearity with low scatter. The derived bimolecular rate coefficients for the TBHP + CH_2OO reaction can be found in Table 4-7, with a recommended value of $(1.10 \pm 0.08) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This result is in reasonable agreement with the absolute rate measurement of $(1.2^{+1.2}_{-0.6}) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ reported by (Caravan et al., 2024).

Table 4-7. Tabulated CI rate coefficients for the *tert*-butyl hydroperoxide, together with analysis parameters. The detailed measurement conditions corresponding to this table can be found in Table 4-3.

No	Target compound	k^a	Method ^b	Reference compound	$k \text{ ref}^c$	Slope ^d
CI-1	$tert$ -butyl hydroperoxide (TBHP) 	$(1.09 \pm 0.12) \times 10^{-13}$	RR	methanol	$(1.16 \pm 0.15) \times 10^{-13}$	0.944 ± 0.016
CI-2		$(1.09 \pm 0.12) \times 10^{-13}$	RR	methanol	$(1.16 \pm 0.15) \times 10^{-13}$	0.946 ± 0.016
CI-3		$(1.12 \pm 0.25) \times 10^{-13}$	RR	2-propanol	$(1.64 \pm 0.25) \times 10^{-13}$	0.685 ± 0.012
CI-4		$(1.17 \pm 0.30) \times 10^{-13}$	RR	2-butanol	$(2.01 \pm 0.30) \times 10^{-13}$	0.581 ± 0.006
		$(1.10 \pm 0.08) \times 10^{-13}$	<i>recommended</i> ^e			

^aUnits of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, errors are reported at weighted averages of reference rate constants and measured slopes. ^b“RR” = relative rate. ^cUnits of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, reference rate coefficients referred from (Wang et al., 2025). ^dMeasured slopes, errors are 2σ . ^eRecommended values are error-weighted means, where multiple measurements are available.

Beyond TBHP measurements, we also attempted to probe the reactivity of α -alkoxyacyl hydroperoxides with CH_2OO . As in previous sections, target ROOHs were *in situ* synthesized via alkene ozonolysis, and CH_2OO was supplied by ethene ozonolysis as the oxidant. A central challenge, however, emerged from the sequential ozonolysis, which led to substantial accumulation of secondary by-products, causing severe spectral interference on the peaks of interest in the PTR-MS and becoming the major obstacle to these measurements. In preliminary experiments, HPMA and HPEA formed from the combination of propene ozonolysis and acetic acid as SCI scavenger were both obscured by interference, preventing reliable analysis. To mitigate this, we turned to use isovaleric acid as precursor, reasoning that its higher molecular weight would yield ROOHs shifted to higher nominal masses, thereby less prone to overlap with interference.

Figure 4-15 illustrates a representative case. In the presence of isovaleric acid, we conducted propene ozonolysis to generate two target ROOHs, hydroperoxymethyl 3-methylbutanoate (HPMMB, red trace) and hydroperoxyethyl 3-methylbutanoate (HPEMB, green trace), with their diagnostic m/z features confirmed in panels b and c. During the *synthesis phase*, propene was added in sufficient excess to produce enough SCI to and consume the acid completely, otherwise residual acid would continue to react with CH_2OO in the *reactivity phase* to reform HPMMB, directly compromising the measurement. Following acid depletion, both ROOHs rose to detectable levels and stabilized. Methanol and 2-

butanol were introduced as reference compounds in the *stabilization phase*, and monitored concurrently.

In the *reactivity phase*, ethene was injected to generate CH₂OO in an ozone-excess background. While the references decayed as expected, both ROOH signals increased instead of showing a clean loss. Notably, a persistent signal on the isovaleric trace (*m/z* 120.102) remained and decreased as the ethene was injected, indicating the presence of an isomeric product. Any such species containing a labile hydrogenous bond or carbonyl group could undergo insertion or addition with CH₂OO, and thereby yielding products at the same nominal mass as the target HPMMB. In addition, the HPEME trace was even more strongly affected, suggesting additional unresolved interference at the current mass resolution.

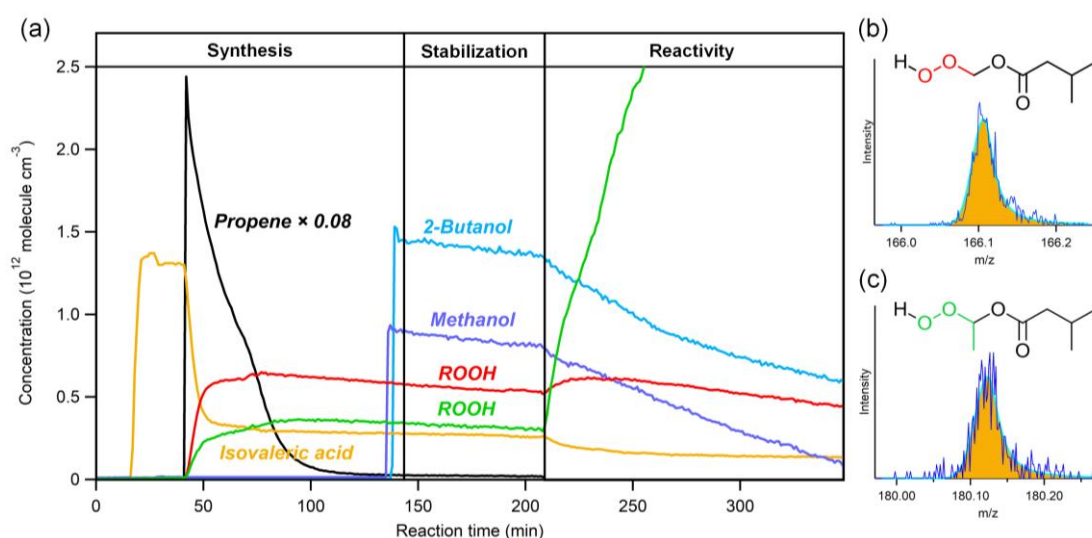


Figure 4-15. Panel (a) Time series of experimental data of an ozonolysis-synthesized α -alkoxyacyl hydroperoxide relative rate experiment, showing the *synthesis*, *stabilization* and *reactivity* phases. SCI relative rate kinetics are obtained during the *reactivity phase*, where SCIs are generated via ethene ozonolysis. Mass spectrum of the SCI insertion product into valeric acid is shown in panel (b). Concentration of the resulting hydroperoxide is estimated through numerical simulation (see Table A4-4 for modelling details). Propene is multiplied by a factor of 0.08 for better visualization

The limitations for the current methodology of our CI experiments arise from two main factors. First, the bimolecular reactions of SCI act as the source of the target ROOHs and as their oxidant, making the kinetic analysis highly susceptible to interference from such isomers sharing the same mass of the

acid precursor. Second, under conditions where numerous secondary products have already accumulated, achieving sufficient CH₂OO flux required substantially increasing ethene ozonolysis input. This inevitably introduced competitive reactions and mass spectral overlap, further compromising the reliability of the measurements. For these reasons, we do not report rate coefficients for the reactions of α -alkoxyacyl hydroperoxides with CH₂OO, and emphasize that such measurements will require cleaner generation/reaction separation strategies or higher-resolution detection techniques in future work.

4.4 Atmospheric implications

As emphasized throughout this thesis, atmospheric oxidation of organic molecules generally proceeds toward progressively higher oxidation states (Kroll et al., 2011). During atmospheric oxidation, –O–O– bonds are prone to arise, and even accumulate, especially when the carbon backbone is enriched in oxygen content, and autoxidation may compete effectively with radical-driven oxidation (Bianchi et al., 2019). Highly oxygenated molecules have been firmly established as key intermediates in the atmosphere, many of which are likely to contain multiple –OOH groups (Barber and Kroll, 2021; Molteni et al., 2019, 2018). The introduction of such substitutions modulates reaction kinetics and alters energetics, for instance by changing bond strengths, the stability of pre-reactive complexes, or the accessibility of reactive sites, thereby reshaping their atmospheric lifetimes and product distributions (Barber and Kroll, 2021). The kinetic data obtained in this study provide a very initial and empirical basis for constraining the atmospheric fate of multifunctional hydroperoxides, allowing us to take these relatively simple ROOHs as a starting point for evaluating their gas-phase behaviour.

Based on the rate coefficients determined in this work, together with estimated contributions from photolysis and wet deposition, Figure 4-16 summarizes the relative importance of five major atmospheric loss pathways for α -alkoxyacyl hydroperoxides. The corresponding atmospheric lifetimes and first-order loss rates are tabulated in Table 4-8. Specifically, the OH and NO₃ loss were calculated using bimolecular rate coefficients for HPMA, with [OH] taken as the global ground-level average of 3×10^6 molecule cm⁻³ (Brasseur and Solomon, 2005) and [NO₃] as a typical nighttime mixing ratio of $5 \times$

10^8 molecule cm^{-3} (Atkinson, 1991). Because measurement of HPMA for Criegee intermediate reactions was not available, TBHP was adopted as the most probable analogy for this purpose. A representative [SCI] of 5×10^4 molecule cm^{-3} (Novelli et al., 2017) was applied, though this value remains highly uncertain and will be discussed further below.

Photolysis rates were calculated by integrating photon fluxes with estimated photolysis quantum yields and absorption cross sections of analogous compounds. We selected 40°N as a representative latitude and simulated typical mid-latitude solar radiation on March 2023 using the Tropospheric Ultraviolet and Visible (TUV) radiation mode. We assumed a quantum yield of unity across the photolysis range because the weak --O--O-- bond is expected to have a low barrier to photodissociation. In addition, due to the lack of direct measurements of the absorption cross section data for the compounds measured in this work, we employed data for hydroxymethyl hydroperoxide as the best analogy to representation (Bauerle and Moortgat, 1999; Keller-Rudek et al., 2013). Contribution of wet deposition was approximated by assuming an atmospheric lifetime of the order of 10 days (Hurley et al., 2004).

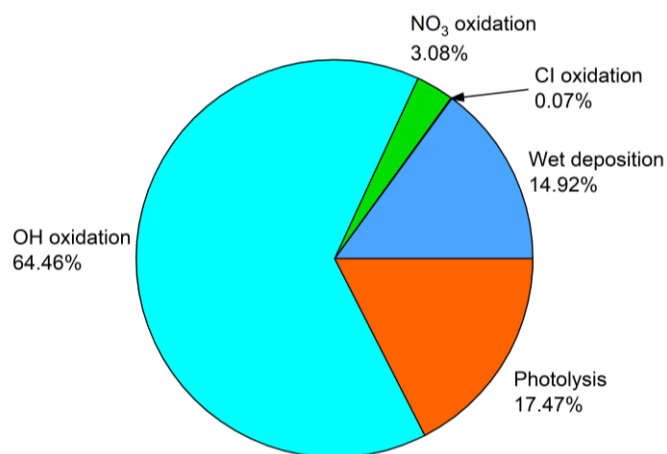


Figure 4-16. Pie chart showing the relative contributions of five major atmospheric removal pathways for hydroperoxymethyl acetate. The calculation is based on first-order decay rates for each loss process in the atmosphere. Typical global average concentrations of atmospheric oxidants are used: $[\text{OH}] = 3 \times 10^6$ molecule cm^{-3} (Brasseur and Solomon, 2005), $[\text{NO}_3] = 5 \times 10^8$ molecule cm^{-3} (Atkinson, 1991), and $[\text{Cl}] = 5 \times 10^4$ molecule cm^{-3} (Novelli et al., 2017). Additional calculation details are provided in the main text.

Overall, we acknowledge that radical concentrations can vary depending on factors such as, the time of the day, the availability of solar radiation, and the geographical location, and that the estimates for photolysis and wet deposition only have limited data available. Therefore, the relative and absolute contributions of these loss pathways to ROOH are not without uncertainties, and should be regarded as an approximation.

Table 4-8. Estimated atmospheric lifetimes, first-order loss rate and fractional contributions of major atmospheric sinks for α -alkoxyacyl hydroperoxide.

Pathway	Lifetime (days)	k' (s^{-1})	Fraction (%)
Photolysis	8.54	1.36E-06	17.47%
OH oxidation	2.31	5.00E-06	64.46%
NO ₃ oxidation	48.41	2.39E-07	3.08%
Criegee oxidation	2104.17	5.50E-09	0.07%
Wet deposition	10.00	1.16E-06	14.92%

The results indicate that OH oxidation is the dominant gas-phase sink for α -alkoxyacyl hydroperoxides, followed by photolysis and wet deposition. From the perspective of reactivity, the bimolecular rate coefficients of HPMA ($1.65 \pm 0.10 \times 10^{-12}$) and HPEA ($2.01 \pm 0.13 \times 10^{-12}$) with OH are not particularly high, but it still appears to be the dominant loss channel comparatively. It can be anticipated that multiphase degradation or partitioning may catch up with, or even overtake gas-phase OH oxidation as the dominant sink for more complex and functionalized ROOHs present in the atmosphere. This is highly relevant to secondary aerosol formation associated with the contributions from highly oxygenated molecules.

NO₃ oxidation plays only a limited role to the total removal of α -alkoxyacyl hydroperoxides, as has been observed for many oxygenated VOCs. However, disregarding substitution effects, the simplest ROOHs that contain only one oxygenated group such as TBHP, exhibit relatively high reactivity toward NO₃ ($\sim 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), comparable to that of aldehydes but much greater than that of alcohols, acids, ketones, esters and ethers. Considering the fact that the NO₃ rate coefficient for HPMA is ~ 33 times lower than that of TBHP, the contribution of NO₃ oxidation would become comparable to OH

oxidation if the calculation is instead performed with TBHP reactivities. This implies that NO_3 may represent an important but underappreciated loss pathways for simple ROOH species.

Recent field observations by Caravan et al., (2024) in the Amazon rainforest provided evidence that sequential CH_2OO insertion into formic acid yielded oligomeric product masses in the form of $\text{HC(O)O(CH}_2\text{OO)}_n\text{H}$, which were detected in both gas and particle phases. These findings suggest that such insertion reactions proceed even under humid conditions and the resulting hydroperoxide are directly relevant to the compounds investigated in this work. However, our results indicate that, in a more comprehensive atmospheric budget, the contribution of Criegee intermediates to ROOH is minor and doesn't appear competitive with other removal pathways. This apparent discrepancy may stem from the tremendous uncertainty in the ambient concentration of SCIs. To date, no reproducible direct measurements of SCI have been achieved, and estimates inferred only by indirect indicators such as sulfuric acid production budgets, unexplained OH reactivity, or instrument background signals, all of which carry significant uncertainties (Novelli et al., 2017). If the observation of Caravan et al., (2024) is taken to be correct, the representative [SCI] of $5 \times 10^4 \text{ molecule cm}^{-3}$ used in the original calculation would need to be at least two orders of magnitude higher to place Criegee intermediate oxidation on a level comparable with the other removal pathways.

4.5 Conclusions

In this study, we targeted two representative ROOH classes: (1) α -alkoxyacyl hydroperoxides that have been generated *in situ* by alkene ozonolysis in the presence of carboxylic acids using a chamber facility, and (2) *tert*-butyl hydroperoxide as a benchmark to supplement the observation. Using a chamber-based relative rate approach, we determined bimolecular rate coefficients with three key atmospheric oxidants (OH, NO_3 and CH_2OO) under dark conditions.

Through this approach, we obtained new kinetic data for the reactions for two representative α -alkoxyacyl hydroperoxides, HPMA and HPEA, with both OH and NO_3 radicals, while their kinetics with CH_2OO are not reported here due to inherent measurement limitations. For TBHP, kinetic data with NO_3 and CH_2OO were also determined and included in the discussion.

Simulated first-order photolysis rates and an approximate contribution from wet deposition were integrated with the experimentally derived oxidation kinetics of OH, NO₃ and CH₂OO to establish five major removal pathways for α -alkoxyacyl hydroperoxides. The results clearly demonstrated the dominant role of OH oxidation. Interestingly, NO₃ exhibited enhanced reactivity toward the simplest hydroperoxides containing only a –OOH functionality, suggesting that NO₃ oxidation may constitute a surprisingly important sink in the atmosphere. In contrast, the contribution of Criegee intermediates to ROOH removal appears to be minor, which is paradoxical, given recent field observations of Criegee intermediate insertion products, and suggest that the ambient [SCI] may need to be reconsidered in the future.

Taken together, these results provide the first systematic datasets on the gas-phase reactivity of hydroperoxides. Starting from these relatively simple ROOH, these measurements represent an essential step toward constraining the lifetime of elusive but important intermediates. We also emphasize the importance of extending laboratory and field studies to more complex and highly functionalized molecules, as a necessary step toward progressively advancing our understanding of their broader atmospheric significance.

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Appendices: Chapter 4

Table A4-1. Details of reaction mechanisms and kinetic parameters contained within the numeric simulations of experimental time-series shown in Figure 4-4, 4-6, 4-8, 4-10, 4-12, 4-13, respectively.

#	Reactions	Rate coefficient	Reference	Comment
Reaction mechanism for the ROOH synthesis shown in Figure 4-4				
R1	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{CH}_2\text{OO} + \text{CH}_3\text{CHO}$	2.10×10^{-18}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R2	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow E\text{-CH}_3\text{CHOO} + \text{HCHO}$	5.25×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R3	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow Z\text{-CH}_3\text{CHOO} + \text{HCHO}$	5.25×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R4	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{OH} + \text{CH}_3\text{CHO}$	6.30×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R5	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{OH} + \text{HCHO}$	3.15×10^{-18}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R6	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{Products} + \text{CH}_3\text{CHO}$	1.26×10^{-18}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R7	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{Products} + \text{HCHO}$	2.31×10^{-18}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R8	$\text{CH}_2\text{OO} + \text{CH}_3\text{C}(\text{O})\text{OH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{OOH}$	1.30×10^{-10}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/CGI_10.pdf
R9	$\text{CH}_3\text{C}(\text{O})\text{OCH}_2\text{OOH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{H} + \text{H}_2\text{O}$	prompt (20%)	(Wang et al., 2025)	Based on our previous observation
R10	$E\text{-CH}_3\text{CHOO} + \text{CH}_3\text{C}(\text{O})\text{OH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OCH}(\text{CH}_3)\text{OOH}$	2.50×10^{-10}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/CGI_27.pdf
R11	$Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{C}(\text{O})\text{OH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OCH}(\text{CH}_3)\text{OOH}$	1.70×10^{-10}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/CGI_27.pdf
R12	$\text{CH}_3\text{C}(\text{O})\text{OCH}(\text{CH}_3)\text{OOH} \rightarrow \text{CH}_3\text{C}(\text{O})\text{OC}(\text{O})\text{CH}_3$	prompt (20%)	(Wang et al., 2025)	Based on our previous observation
R13	$\text{CH}_2\text{OO} + \text{HCHO} \rightarrow \text{SOZ}$	3.48×10^{-12}	(Enders et al., 2024)	
R14	$\text{CH}_2\text{OO} + \text{CH}_3\text{CHO} \rightarrow \text{SOZ}$	1.51×10^{-12}	(Enders et al., 2024)	
R15	$E\text{-CH}_3\text{CHOO} + \text{HCHO} \rightarrow \text{SOZ}$	2.11×10^{-13}	(Jiang et al., 2024)	Analogy to the reaction $Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO}$
R16	$E\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO} \rightarrow \text{SOZ}$	2.11×10^{-13}	(Jiang et al., 2024)	Analogy to the reaction $Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO}$

R17	$\text{Z-CH}_3\text{CHOO} + \text{HCHO} \rightarrow \text{SOZ}$	2.11×10^{-13}	(Jiang et al., 2024)	Analogy to the reaction $\text{Z-CH}_3\text{CHOO} + \text{CH}_3\text{CHO}$
R18	$\text{Z-CH}_3\text{CHOO} + \text{CH}_3\text{CHO} \rightarrow \text{SOZ}$	2.11×10^{-13}	(Jiang et al., 2024)	Analogy to the reaction $\text{Z-CH}_3\text{CHOO} + \text{CH}_3\text{CHO}$
R19	$\text{OH} + \text{CH}_3\text{C(O)OH} \rightarrow \text{CH}_3\text{C(O)O} + \text{H}_2\text{O}$	4.83×10^{-13}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC36.pdf
R20	$\text{OH} + \text{CH}_3\text{C(O)OH} \rightarrow \text{CH}_2\text{C(O)OH} + \text{H}_2\text{O}$	2.07×10^{-13}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC36.pdf
R21	$\text{OH} + \text{C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_6\text{OH}$	2.09×10^{-11}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC5.pdf
R22	$\text{OH} + \text{HCHO} \rightarrow \text{HCO} + \text{H}_2\text{O}$	2.50×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC11.pdf
R23	$\text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O}$	1.43×10^{-11}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC12.pdf
R24	$\text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_2\text{CHO} + \text{H}_2\text{O}$	7.50×10^{-13}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC12.pdf
R25	$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	5.20×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/R_Oxygen10.pdf
R26	$\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{C(O)O}_2$	5.10×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/R_Oxygen11.pdf
R27	$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	7.30×10^{-14}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx13.pdf
R28	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$	2.00×10^{-15}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx15.pdf
R29	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	1.60×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx14.pdf
R30	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	1.00×10^{-10}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx11.pdf
R31	$\text{OH} + \text{CH}_3\text{C(O)OCH}_2\text{OOH} \rightarrow \text{Products}$	1.67×10^{-12}	this work	
R32	$\text{OH} + \text{CH}_3\text{C(O)OCH}(\text{CH}_3)\text{OOH} \rightarrow \text{Products}$	2.03×10^{-12}	this work	
R33	$\text{OH} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R34	$\text{HO}_2 \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R35	$\text{CH}_2\text{OO} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R36	$\text{E-CH}_3\text{CHOO} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments

R37	$Z\text{-CH}_3\text{CHOO} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
Reaction mechanism for the ROOH reactivity shown in Figure 4-6				
R1	$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	1.90×10^{-14}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/NOx24.pdf
R2	$\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2$	3.50×10^{-17}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/NOx28.pdf
R3	$\text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5$	1.90×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/NOx31.pdf
R4	$\text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2$	4.40×10^{-2}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/NOx32.pdf
R5	$\text{NO} + \text{O}_2 \rightarrow \text{NO}_2$	3.95×10^{-38}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/NOx23.pdf
R6	$\text{NO} + \text{NO}_2 \rightarrow \text{N}_2\text{O}_3$	7.50×10^{-15}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/NOx25.pdf
R7	$\text{N}_2\text{O}_3 \rightarrow \text{NO} + \text{NO}_2$	3.60×10^5	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/NOx26.pdf
R8	$\text{NO}_2 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$	2.30×10^{-14}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/NOx29.pdf
R9	$\text{N}_2\text{O}_4 \rightarrow \text{NO}_2 + \text{NO}_2$	1.00×10^5	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/NOx30.pdf
R10	$n\text{-C}_3\text{H}_7\text{CHO} + \text{NO}_3 \rightarrow n\text{-C}_3\text{H}_7\text{C(O)O}_2 + \text{HNO}_3$	1.10×10^{-14}	(McGillen et al., 2020)	
R11	$n\text{-C}_3\text{H}_7\text{C(O)O}_2 + \text{NO}_2 \rightarrow n\text{-C}_3\text{H}_7\text{C(O)O}_2\text{NO}_2$	8.90×10^{-12}	(IUPAC, 2025)	Analogy to the reaction of $\text{CH}_3\text{C(O)O}_2 + \text{NO}_2$ https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_14.pdf
R12	$(\text{CH}_3)_3\text{COOH} + \text{NO}_3 \rightarrow (\text{CH}_3)_3\text{CO}_2 + \text{HNO}_3$	1.70×10^{-14}	this work	
R13	$(\text{CH}_3)_3\text{CO}_2 + \text{NO}_2 \rightarrow (\text{CH}_3)_3\text{CO}_2\text{NO}_2$	5.10×10^{-12}	(IUPAC, 2025)	Analogy to the reaction of $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2$ https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_11.pdf
R14	$n\text{-C}_3\text{H}_7\text{C(O)O}_2 + n\text{-C}_3\text{H}_7\text{C(O)O}_2 \rightarrow n\text{-C}_3\text{H}_7\text{C(O)O} + n\text{-C}_3\text{H}_7\text{C(O)O}$	1.70×10^{-11}	(IUPAC, 2025)	Analogy to the reaction of $\text{C}_2\text{H}_5\text{C(O)O}_2 + \text{C}_2\text{H}_5\text{C(O)O}_2$ https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_47.pdf
R15	$(\text{CH}_3)_3\text{CO}_2 + (\text{CH}_3)_3\text{CO}_2 \rightarrow (\text{CH}_3)_3\text{CO} + (\text{CH}_3)_3\text{CO}$	2.10×10^{-17}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_42.pdf
R16	$n\text{-C}_3\text{H}_7\text{C(O)O}_2 + (\text{CH}_3)_3\text{CO}_2 \rightarrow n\text{-C}_3\text{H}_7\text{C(O)O} + (\text{CH}_3)_3\text{CO}$	2.40×10^{-12}	(IUPAC, 2025)	Analogy to the reaction of $\text{C}_2\text{H}_5\text{O}_2 + \text{C}_2\text{H}_5\text{C(O)O}_2$

				https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_48.pdf
R17	$n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{O}_2\text{NO}_2 \rightarrow n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{OO} + \text{NO}_2$	3.60×10^{-4}	(IUPAC, 2025)	Analogy to the reaction of $\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2\text{NO}_2 + \text{M}$ https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_16.pdf
R18	$(\text{CH}_3)_3\text{CO}_2\text{NO}_2 \rightarrow (\text{CH}_3)_3\text{CO}_2 + \text{NO}_2$	3.4	(IUPAC, 2025)	Analogy to the reaction of $\text{C}_2\text{H}_5\text{O}_2\text{NO}_2 + \text{M}$ https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_12.pdf
R19	$n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{O}_2 + \text{NO}_3 \rightarrow n\text{-C}_3\text{H}_7\text{CO}_2 + \text{NO}_2 + \text{O}_2$	4.00×10^{-12}	(IUPAC, 2025)	Analogy to the reaction of $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_3$ https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_21.pdf
R20	$(\text{CH}_3)_3\text{CO}_2 + \text{NO}_3 \rightarrow (\text{CH}_3)_3\text{CO} + \text{NO}_2 + \text{O}_2$	2.30×10^{-12}	(IUPAC, 2025)	Analogy to the reaction of $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_3$ https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_20.pdf
R21	$n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{O}_2 + \text{O}_3 \rightarrow n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{O} + \text{O}_2$	1.00×10^{-17}	(Tyndall et al., 1998)	Analogy to the reaction of $\text{CH}_3\text{OO} + \text{O}_3$
R22	$(\text{CH}_3)_3\text{CO}_2 + \text{O}_3 \rightarrow (\text{CH}_3)_3\text{CO} + \text{O}_2$	1.00×10^{-17}	(Tyndall et al., 1998)	Analogy to the reaction of $\text{CH}_3\text{OO} + \text{O}_3$
R23	$n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{O} + \text{NO}_2 \rightarrow n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{ONO}_2$	2.80×10^{-11}	(IUPAC, 2025)	Analogy to the reaction of $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2$ https://iupac-aeris.ipsl.fr/datasheets/pdf/RO_18.pdf
R24	$(\text{CH}_3)_3\text{CO} + \text{NO}_2 \rightarrow (\text{CH}_3)_3\text{CONO}_2$	2.80×10^{-11}	(IUPAC, 2025)	Analogy to the reaction of $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2$ https://iupac-aeris.ipsl.fr/datasheets/pdf/RO_18.pdf
R25	$n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{O} + \text{O}_3 \rightarrow n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{O}_2 + \text{O}_2$	2.53×10^{-14}	(Albaladejo et al., 2002)	Analogy to the reaction of $\text{C}_2\text{H}_5\text{O}_2 + \text{O}_3$
R26	$(\text{CH}_3)_3\text{CO} + \text{O}_3 \rightarrow (\text{CH}_3)_3\text{CO}_2 + \text{O}_2$	2.53×10^{-14}	(Albaladejo et al., 2002)	Analogy to the reaction of $\text{C}_2\text{H}_5\text{O}_2 + \text{O}_3$
R27	$n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{O} \rightarrow n\text{-C}_3\text{H}_7 + \text{CO}_2$	5.43×10^8	(Tsang, 1987)	Analogy to the reaction of $\text{CH}_3\text{C}(\text{O})\text{O}$ decarboxylation
R28	$n\text{-C}_3\text{H}_7 + \text{O}_2 \rightarrow n\text{-C}_3\text{H}_7\text{O}_2$	6.00×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/R_Oxygen5.pdf
R29	$n\text{-C}_3\text{H}_7\text{O}_2 + n\text{-C}_3\text{H}_7\text{O}_2 \rightarrow n\text{-C}_3\text{H}_7\text{OH} + \text{C}_2\text{H}_5\text{CHO}$	1.32×10^{-13}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_32.pdf
R30	$n\text{-C}_3\text{H}_7\text{O}_2 + n\text{-C}_3\text{H}_7\text{O}_2 \rightarrow n\text{-C}_3\text{H}_7\text{O} + n\text{-C}_3\text{H}_7\text{O}$	1.68×10^{-13}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_32.pdf
R31	$n\text{-C}_3\text{H}_7\text{O}_2 + \text{NO}_2 \rightarrow n\text{-C}_3\text{H}_7\text{O}_2\text{NO}_2$	5.10×10^{-12}	(IUPAC, 2025)	Analogy to the reaction of $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2$ https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_11.pdf

R32	$n\text{-C}_3\text{H}_7\text{O} + \text{O}_2 \rightarrow n\text{-C}_2\text{H}_5\text{CHO} + \text{HO}_2$	1.00×10^{-14}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/RO_3.pdf
R33	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	1.60×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx14.pdf
R34	$\text{HO}_2 + \text{NO}_2 \rightarrow \text{HO}_2\text{NO}_2$	7.50×10^{-13}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/NOx16.pdf
R35	$\text{HO}_2\text{NO}_2 \rightarrow \text{HO}_2 + \text{NO}_2$	6.20×10^{-2}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/NOx17.pdf
R36	$n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{O}_2 + \text{HO}_2 \rightarrow n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{O}_2\text{H} + \text{O}_2$	6.90×10^{-12}	(IUPAC, 2025)	Analogy to the reaction of $\text{C}_2\text{H}_5\text{O}_2 + \text{HO}_2$ https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC53.pdf
R37	$(\text{CH}_3)_3\text{CO}_2 + \text{HO}_2 \rightarrow (\text{CH}_3)_3\text{CO}_2\text{H} + \text{O}_2$	6.90×10^{-12}	(IUPAC, 2025)	Analogy to the reaction of $\text{C}_2\text{H}_5\text{O}_2 + \text{HO}_2$ https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC53.pdf
R38	$\text{NO}_3 \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R39	$n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{O}_2 \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R40	$(\text{CH}_3)_3\text{CO}_2 \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R41	$\text{HO}_2 \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R42	$n\text{-C}_3\text{H}_7\text{C}(\text{O})\text{O} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R43	$(\text{CH}_3)_3\text{CO} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R44	$n\text{-C}_3\text{H}_7\text{O}_2 \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R45	$n\text{-C}_3\text{H}_7\text{O} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
Reaction mechanism for the ROOH synthesis shown in Figure 4-8				
R1	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{CH}_2\text{OO} + \text{CH}_3\text{CHO}$	2.10×10^{-18}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R2	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow E\text{-CH}_3\text{CHOO} + \text{HCHO}$	5.25×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R3	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow Z\text{-CH}_3\text{CHOO} + \text{HCHO}$	5.25×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R4	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{OH} + \text{CH}_3\text{CHO}$	6.30×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf

R5	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{OH} + \text{HCHO}$	3.15×10^{-18}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R6	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{Products} + \text{CH}_3\text{CHO}$	1.26×10^{-18}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R7	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{Products} + \text{HCHO}$	2.31×10^{-18}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R8	$\text{CH}_2\text{OO} + \text{CH}_3\text{C(O)OH} \rightarrow \text{CH}_3\text{C(O)OCH}_2\text{OOH}$	1.30×10^{-10}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/CGI_10.pdf
R9	$\text{CH}_3\text{C(O)OCH}_2\text{OOH} \rightarrow \text{CH}_3\text{C(O)OC(O)H} + \text{H}_2\text{O}$	prompt (20%)	(Wang et al., 2025)	Based on our previous observation
R10	$E\text{-CH}_3\text{CHOO} + \text{CH}_3\text{C(O)OH} \rightarrow \text{CH}_3\text{C(O)OCH}(\text{CH}_3)\text{OOH}$	2.50×10^{-10}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/CGI_27.pdf
R11	$Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{C(O)OH} \rightarrow \text{CH}_3\text{C(O)OCH}(\text{CH}_3)\text{OOH}$	1.70×10^{-10}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/CGI_27.pdf
R12	$\text{CH}_3\text{C(O)OCH}(\text{CH}_3)\text{OOH} \rightarrow \text{CH}_3\text{C(O)OC(O)CH}_3$	prompt (20%)	(Wang et al., 2025)	Based on our previous observation
R13	$\text{CH}_2\text{OO} + \text{HCHO} \rightarrow \text{SOZ}$	3.48×10^{-12}	(Enders et al., 2024)	
R14	$\text{CH}_2\text{OO} + \text{CH}_3\text{CHO} \rightarrow \text{SOZ}$	1.51×10^{-12}	(Enders et al., 2024)	
R15	$E\text{-CH}_3\text{CHOO} + \text{HCHO} \rightarrow \text{SOZ}$	2.11×10^{-13}	(Jiang et al., 2024)	Analogy to the reaction $Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO}$
R16	$E\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO} \rightarrow \text{SOZ}$	2.11×10^{-13}	(Jiang et al., 2024)	Analogy to the reaction $Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO}$
R17	$Z\text{-CH}_3\text{CHOO} + \text{HCHO} \rightarrow \text{SOZ}$	2.11×10^{-13}	(Jiang et al., 2024)	Analogy to the reaction $Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO}$
R18	$Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO} \rightarrow \text{SOZ}$	2.11×10^{-13}	(Jiang et al., 2024)	Analogy to the reaction $Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO}$
R19	$\text{OH} + \text{CH}_3\text{C(O)OH} \rightarrow \text{CH}_3\text{C(O)O} + \text{H}_2\text{O}$	4.83×10^{-13}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC36.pdf
R20	$\text{OH} + \text{CH}_3\text{C(O)OH} \rightarrow \text{CH}_2\text{C(O)OH} + \text{H}_2\text{O}$	2.07×10^{-13}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC36.pdf
R21	$\text{OH} + \text{C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_6\text{OH}$	2.09×10^{-11}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC5.pdf
R22	$\text{OH} + \text{HCHO} \rightarrow \text{HCO} + \text{H}_2\text{O}$	2.50×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC11.pdf
R23	$\text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O}$	1.43×10^{-11}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC12.pdf

R24	$\text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_2\text{CHO} + \text{H}_2\text{O}$	7.50×10^{-13}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC12.pdf
R25	$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	5.20×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/R_Oxygen10.pdf
R26	$\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{C(O)O}_2$	5.10×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/R_Oxygen11.pdf
R27	$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	7.30×10^{-14}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx13.pdf
R28	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$	2.00×10^{-15}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx15.pdf
R29	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	1.60×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx14.pdf
R30	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	1.00×10^{-10}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx11.pdf
R31	$\text{OH} + \text{CH}_3\text{C(O)OCH}_2\text{OOH} \rightarrow \text{Products}$	1.67×10^{-12}	this work	
R32	$\text{OH} + \text{CH}_3\text{C(O)OCH}(\text{CH}_3)\text{OOH} \rightarrow \text{Products}$	2.03×10^{-12}	this work	
R33	$\text{OH} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R34	$\text{HO}_2 \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R35	$\text{CH}_2\text{OO} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R36	$E\text{-CH}_3\text{CHOO} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R37	$Z\text{-CH}_3\text{CHOO} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
Reaction mechanism for the ROOH synthesis shown in Figure 4-10				
R1	$\text{C}_2\text{H}_4 + \text{O}_3 \rightarrow \text{CH}_2\text{OO} + \text{HCHO}$	6.51×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC5.pdf
R2	$\text{C}_2\text{H}_4 + \text{O}_3 \rightarrow \text{HC(O)OH} + \text{HCHO}$	1.09×10^{-19}	(Leather et al., 2012)	HC(O)OH yield under dry conditions
R3	$\text{C}_2\text{H}_4 + \text{O}_3 \rightarrow \text{OH} + \text{HCHO} + \text{HCO}$	2.64×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC5.pdf
R4	$\text{C}_2\text{H}_4 + \text{O}_3 \rightarrow 2\text{H} + \text{HCHO}$	4.50×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC5.pdf
R5	$\text{C}_2\text{H}_4 + \text{O}_3 \rightarrow \text{Products} + \text{HCHO}$	7.75×10^{-20}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC5.pdf
R6	$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	5.20×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/R_Oxygen10.pdf

R7	$\text{H} + \text{O}_2 \rightarrow \text{HO}_2$	1.00×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx2.pdf
R8	$\text{CH}_2\text{OO} + \text{HCHO} \rightarrow \text{FSOZ}$	3.48×10^{-12}	(Enders et al., 2024)	
R9	$\text{CH}_2\text{OO} + \text{HC(O)OH} \rightarrow \text{HC(O)OCH}_2\text{OOH}$	1.10×10^{-10}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/CGI_11.pdf
R10	$\text{CH}_2\text{OO} + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OCH}_2\text{OOH}$	1.06×10^{-13}	(Wang et al., 2025)	
R11	$\text{CH}_3\text{OCH}_2\text{OOH} \rightarrow \text{CH}_3\text{OCHO}$	prompt (40%)	(Wang et al., 2025)	Based on our previous observation
R12	$\text{CH}_2\text{OO} + (\text{CH}_3)_3\text{COOH} \rightarrow (\text{CH}_3)_3\text{COOCH}_2\text{OOH}$	1.10×10^{-13}	this work	
R13	$(\text{CH}_3)_3\text{COOCH}_2\text{OOH} \rightarrow (\text{CH}_3)_3\text{COOCHO}$	prompt (40%)	(Wang et al., 2025)	Assumed to be analogous to R11
R14	$\text{CH}_2\text{OO} + \text{ROOH} \rightarrow \text{ROO}(\text{CH}_2\text{OO})\text{H}$	1.20×10^{-13}	(Caravan et al., 2024)	Analogy to the reaction $\text{CH}_2\text{OO} + (\text{CH}_3)_3\text{COOH}$
R15	$\text{CH}_2\text{OO} + \text{ROO}(\text{CH}_2\text{OO})\text{H} \rightarrow \text{ROO}(\text{CH}_2\text{OO})_2\text{H}$	1.20×10^{-13}	(Caravan et al., 2024)	Analogy to the reaction $\text{CH}_2\text{OO} + (\text{CH}_3)_3\text{COOH}$
R16	$\text{OH} + \text{HCHO} \rightarrow \text{HCO} + \text{H}_2\text{O}$	8.50×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC11.pdf
R17	$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	7.30×10^{-14}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx13.pdf
R18	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$	2.00×10^{-15}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx15.pdf
R19	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	1.60×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx14.pdf
R20	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	1.10×10^{-10}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx11.pdf
R21	$\text{OH} + c\text{-C}_6\text{H}_{12} \rightarrow c\text{-C}_6\text{H}_{11}\text{O}_2$	6.69×10^{-12}		
R22	$c\text{-C}_6\text{H}_{11}\text{O}_2 + c\text{-C}_6\text{H}_{11}\text{O}_2 \rightarrow c\text{-C}_6\text{H}_{11}\text{O} + c\text{-C}_6\text{H}_{11}\text{O} + \text{O}_2$	8.53×10^{-15}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_26.pdf
R23	$c\text{-C}_6\text{H}_{11}\text{O}_2 + c\text{-C}_6\text{H}_{11}\text{O}_2 \rightarrow c\text{-(CH}_2)_5\text{CO} + c\text{-C}_6\text{H}_{11}\text{OH} + \text{O}_2$	2.09×10^{-14}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/ROO_26.pdf
R24	$c\text{-C}_6\text{H}_{11}\text{O}_2 + \text{HO}_2 \rightarrow c\text{-C}_6\text{H}_{11}\text{OOH} + \text{O}_2$	6.90×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC53.pdf
R25	$c\text{-C}_6\text{H}_{11}\text{O}_2 + \text{O}_3 \rightarrow c\text{-C}_6\text{H}_{11}\text{O} + \text{O}_2$	1.00×10^{-17}	(Tyndall et al., 1998)	Analogy to the reaction $\text{CH}_3\text{OO} + \text{CH}_3\text{OO}$
R26	$c\text{-C}_6\text{H}_{11}\text{O}_2 + \text{OH} \rightarrow c\text{-C}_6\text{H}_{11}\text{O} + \text{HO}_2$	8.60×10^{-11}	(Fittschen, 2019)	Analogy to the reaction $\text{CH}_3\text{OO} + \text{OH}$

R27	$c\text{-C}_6\text{H}_{11}\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{O}_2$	7.00×10^{-12}	(Fittschen, 2019)	Analogy to the reaction $\text{CH}_3\text{OO} + \text{OH}$
R28	$c\text{-C}_6\text{H}_{11}\text{O}_2 + \text{OH} \rightarrow c\text{-C}_6\text{H}_{11}\text{OOOH}$	7.00×10^{-12}	(Fittschen, 2019)	Analogy to the reaction $\text{CH}_3\text{OO} + \text{OH}$
R29	$c\text{-C}_6\text{H}_{11}\text{O} + \text{O}_3 \rightarrow c\text{-C}_6\text{H}_{11}\text{O}_2 + \text{O}_2$	2.53×10^{-14}	(Albaladejo et al., 2002)	Analogy to the reaction $\text{CH}_3 + \text{O}_3$
R30	$c\text{-C}_6\text{H}_{11}\text{O} + \text{O}_2 \rightarrow c\text{-(CH}_2)_5\text{CO} + \text{HO}_2$	1.00×10^{-14}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/RO_3.pdf
R31	$\text{CH}_2\text{OO} + c\text{-C}_6\text{H}_{11}\text{OH} \rightarrow \text{ROOH}$	1.00×10^{-13}	(McGillen et al., 2020)	Analogy to the reaction $\text{CH}_2\text{OO} + \text{CH}_3\text{OH}$
R32	$\text{CH}_2\text{OO} + c\text{-(CH}_2)_5\text{CO} \rightarrow \text{SOZ}$	4.00×10^{-13}	(Cornwell et al., 2021)	Analogy to the reaction $\text{CH}_2\text{OO} + (\text{CH}_3)_2\text{CO}$
R33	$\text{CH}_2\text{OO} + \text{C}_2\text{H}_4 \rightarrow \text{SOZ}$	7.00×10^{-16}	(Buras et al., 2014)	
R34	$\text{C}_2\text{H}_4 + \text{OH} \rightarrow \text{HCHO} + \text{HCHO}$	7.80×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC3.pdf
R35	$\text{FSOZ} \rightarrow \text{CH}_2\text{OO} + \text{HCHO}$	2.00×10^{-3}	(Wang et al., 2025)	Based on our previous observation
R36	$\text{OH} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R37	$\text{HO}_2 \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R38	$\text{CH}_2\text{OO} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R39	$c\text{-C}_6\text{H}_{11}\text{O}_2 \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R40	$c\text{-C}_6\text{H}_{11}\text{O} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
Reaction mechanism for the ROOH synthesis shown in Figure 4-12				
R1	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{CH}_2\text{OO} + \text{CH}_3\text{CHO}$	2.10×10^{-18}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R2	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow E\text{-CH}_3\text{CHOO} + \text{HCHO}$	5.25×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R3	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow Z\text{-CH}_3\text{CHOO} + \text{HCHO}$	5.25×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R4	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{OH} + \text{CH}_3\text{CHO}$	6.30×10^{-19}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R5	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{OH} + \text{HCHO}$	3.15×10^{-18}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf

R6	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{Products} + \text{CH}_3\text{CHO}$	1.26×10^{-18}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R7	$\text{C}_3\text{H}_6 + \text{O}_3 \rightarrow \text{Products} + \text{HCHO}$	2.31×10^{-18}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/Ox_VOC6.pdf
R8	$\text{CH}_2\text{OO} + (\text{CH}_3)_2\text{CH}_2\text{C}(\text{O})\text{OH} \rightarrow (\text{CH}_3)_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{OOH}$	2.76×10^{-10}	(IUPAC, 2025)	Based on our result in Chapter 3
R9	$(\text{CH}_3)_2\text{CH}_2\text{C}(\text{O})\text{OCH}_2\text{OOH} \rightarrow (\text{CH}_3)_2\text{CH}_2\text{C}(\text{O})\text{OC}(\text{O})\text{H} + \text{H}_2\text{O}$	prompt (20%)	(Wang et al., 2025)	Based on our previous observation
R10	$E\text{-CH}_3\text{CHOO} + (\text{CH}_3)_2\text{CH}_2\text{C}(\text{O})\text{OH} \rightarrow (\text{CH}_3)_2\text{CH}_2\text{C}(\text{O})\text{OCH}(\text{CH}_3)\text{OOH}$	2.50×10^{-10}	(IUPAC, 2025)	Analogy to the reaction of $E\text{-CH}_3\text{CHOO} + \text{CH}_3\text{C}(\text{O})\text{OH}$ https://iupac-aeris.ipsl.fr/datasheets/pdf/CGI_27.pdf
R11	$Z\text{-CH}_3\text{CHOO} + (\text{CH}_3)_2\text{CH}_2\text{C}(\text{O})\text{OH} \rightarrow (\text{CH}_3)_2\text{CH}_2\text{C}(\text{O})\text{OCH}(\text{CH}_3)\text{OOH}$	1.70×10^{-10}	(IUPAC, 2025)	Analogy to the reaction of $E\text{-CH}_3\text{CHOO} + \text{CH}_3\text{C}(\text{O})\text{OH}$ https://iupac-aeris.ipsl.fr/datasheets/pdf/CGI_27.pdf
R12	$(\text{CH}_3)_2\text{CH}_2\text{C}(\text{O})\text{OCH}(\text{CH}_3)\text{OOH} \rightarrow (\text{CH}_3)_2\text{CH}_2\text{C}(\text{O})\text{OC}(\text{O})\text{CH}_3$	prompt (20%)	(Wang et al., 2025)	Based on our previous observation
R13	$\text{CH}_2\text{OO} + \text{HCHO} \rightarrow \text{SOZ}$	3.48×10^{-12}	(Enders et al., 2024)	
R14	$\text{CH}_2\text{OO} + \text{CH}_3\text{CHO} \rightarrow \text{SOZ}$	1.51×10^{-12}	(Enders et al., 2024)	
R15	$E\text{-CH}_3\text{CHOO} + \text{HCHO} \rightarrow \text{SOZ}$	2.11×10^{-13}	(Jiang et al., 2024)	Analogy to the reaction $Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO}$
R16	$E\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO} \rightarrow \text{SOZ}$	2.11×10^{-13}	(Jiang et al., 2024)	Analogy to the reaction $Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO}$
R17	$Z\text{-CH}_3\text{CHOO} + \text{HCHO} \rightarrow \text{SOZ}$	2.11×10^{-13}	(Jiang et al., 2024)	Analogy to the reaction $Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO}$
R18	$Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO} \rightarrow \text{SOZ}$	2.11×10^{-13}	(Jiang et al., 2024)	Analogy to the reaction $Z\text{-CH}_3\text{CHOO} + \text{CH}_3\text{CHO}$
R19	$\text{OH} + (\text{CH}_3)_2\text{CH}_2\text{C}(\text{O})\text{OH} \rightarrow \text{Products}$	6.90×10^{-13}	(IUPAC, 2025)	Analogy to the reaction of $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{OH}$ https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC36.pdf
R20	$\text{OH} + \text{C}_3\text{H}_6 \rightarrow \text{C}_3\text{H}_6\text{OH}$	2.09×10^{-11}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC5.pdf
R21	$\text{OH} + \text{HCHO} \rightarrow \text{HCO} + \text{H}_2\text{O}$	2.50×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC11.pdf
R22	$\text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_3\text{CO} + \text{H}_2\text{O}$	1.43×10^{-11}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC12.pdf

R23	$\text{OH} + \text{CH}_3\text{CHO} \rightarrow \text{CH}_2\text{CHO} + \text{H}_2\text{O}$	7.50×10^{-13}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx_VOC12.pdf
R24	$\text{HCO} + \text{O}_2 \rightarrow \text{CO} + \text{HO}_2$	5.20×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/R_Oxygen10.pdf
R25	$\text{CH}_3\text{CO} + \text{O}_2 \rightarrow \text{CH}_3\text{C(O)O}_2$	5.10×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/R_Oxygen11.pdf
R26	$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$	7.30×10^{-14}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx13.pdf
R27	$\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$	2.00×10^{-15}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx15.pdf
R28	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	1.60×10^{-12}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx14.pdf
R29	$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$	1.00×10^{-10}	(IUPAC, 2025)	https://iupac-aeris.ipsl.fr/datasheets/pdf/HOx11.pdf
R30	$\text{OH} + (\text{CH}_3)_2\text{CH}_2\text{C(O)OCH}_2\text{OOH} \rightarrow \text{Products}$	1.67×10^{-12}	this work	Analogy to the reaction of OH + HPMA
R31	$\text{OH} + (\text{CH}_3)_2\text{CH}_2\text{C(O)OCH}(\text{CH}_3)\text{OOH} \rightarrow \text{Products}$	2.03×10^{-12}	this work	Analogy to the reaction of OH + HPEA
R32	$\text{OH} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R33	$\text{HO}_2 \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R34	$\text{CH}_2\text{OO} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R35	$E\text{-CH}_3\text{CHOO} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments
R36	$Z\text{-CH}_3\text{CHOO} \rightarrow \text{wall}$	2.00×10^{-2}		Constrained from previous HELIOS characterization experiments

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Chapter 5:

Conclusion and perspectives

Conclusion and perspectives

I began this thesis by providing a systematic overview of the sources and sinks of atmospheric trace constituents in Chapter 1, and by doing that I pointed to a key issue in atmospheric chemistry that the chemistry of multifunctional molecules produced during multigenerational oxidation processes remain poorly explored. These complex reactions play important roles in atmospheric transformation as many of their consequences are often associated with secondary organic aerosol formation and greenhouse gas emissions. Gaining a deep understanding of the reaction kinetics is a crucial step, because they will define the competition between different atmospheric transformation processes, thus providing a more accurate assessment of secondary chemical processes initiated by anthropogenic and biogenic emissions.

In this context, I performed a systematic photochemical investigation of CF_3CHO (refer to Chapter 2), a key degradation intermediate of anthropogenic fluorinated gases, with particular attention to its potential role as an indirect source of CHF_3 , one of the most potent greenhouse gases. Through a series of single-wavelength and broadband UV photolysis experiments, I quantitatively evaluated the photolysis behaviour of CF_3CHO and its potential to generate CHF_3 . Single-wavelength measurements were found to provide a more suitable and practical approach, allowing me to parameterize the wavelength dependence of both the photolysis quantum yield of CF_3CHO and the product yield of CHF_3 using simple sigmoidal expressions. To my best knowledge, this study provides the first wavelength dependent parameterization for CHF_3 product yield.

These parameterizations were then incorporated into the Stern-Volmer analysis reported by (Van Hoomissen et al., 2025) to characterize the pressure dependence under atmospherically relevant conditions. The oxidation losses of CF_3CHO were also characterized by applying the temperature-dependent rate coefficient for the reaction of $\text{CF}_3\text{CHO} + \text{OH}$ (McGillen et al., 2020), together with theoretical rate coefficient for the reaction of $\text{CF}_3\text{CHO} + \text{HO}_2$ (Long et al., 2022). Based on these analyses, I established that photolysis dominates the removal of CF_3CHO and presented its corresponding molar yield of CHF_3 across altitudes throughout both the troposphere and stratosphere.

Molar yields of CHF_3 across stratospheric altitudes were shown to be at least two orders of magnitude higher than those in the troposphere, underscoring the fact that the contribution of CF_3CHO photolysis to the indirect GWP depends critically on the altitude at which photolysis occurs. By superimposing the atmospheric lifetimes of representative F-gases onto the average age of air, I was able to assess the capacity of these CF_3CHO precursors to undergo vertical transport within the atmosphere. HFOs containing C=C double bonds are rapidly oxidized in the troposphere, resulting in a very limited indirect GWP. However, certain longer-lived F-gases such as HFCs, HCFCs, halons and HFEs are capable of migrating to the stratosphere and degrading to produce CF_3CHO , thereby leading to a more significant increase of indirect GWP. Taking HFC-143a as an example, despite only about 10% of the total being consumed throughout the stratosphere, even so, the associated indirect GWP still shows only a minor increase. However, it should be noted that the oxidation and photolysis of fluorochemicals leads to a variety of other chemical products, and whereas perhaps the formation of CHF_3 is not very significant, other persistent products may be formed and studies should continue on the fate of fluorochemicals entering our environment.

In chapter 3, this thesis developed and validated a chamber-based relative rate approach for determining the gas-phase kinetics of stabilized Criegee intermediates. Using ethene as a symmetric precursor to generate CH_2OO , I determined the bimolecular rate coefficients for its reactions with a series of acids and alcohols. All relative rate plots exhibited good linearity, and the results showed high consistency and reproducibility across different experiments, with the derived rate coefficients in reasonable agreement with absolute measurements reported in the literature. Compared to absolute rate methods that rely on *gem*-diiodoalkane precursors, this approach offers notable advantages in that it requires no specialized synthetic precursors, allows direct experimentation in large-volume chambers, and can handle less volatile or multifunctional co-reactants. The absolute methods rely on the measurement of the temporal decay of the Criegee intermediate, and it is the product of reactant concentration and its reactivity with the SCI that defines this decay in units of s^{-1} . The maximum possible decay rate is therefore limited by both the rate coefficient and the saturation vapour pressure of the co-reactant. In practice, it is prohibitively difficult to reach the saturation vapour pressure in a flowing system, since long time periods are necessary to achieve equilibrium, and also because other

gases are needed in the flow (i.e., carrier gas, CH₂I₂ and O₂). According to our knowledge the lowest vapour pressure and reactivity combinations that have so far been attempted are from (Cornwell et al., 2024), who studied hydroxyacetone (vp = 1.74 Torr, $k_{298} = 1.02 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and 4-hydroxy-2-butanone (vp = 0.857 Torr, $k_{298} = 1.05 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This leads to maximum possible loss-rates of ~60,000 and 30,000 s⁻¹, respectively. By contrast, in my study of 1-hexanol, vp = 0.881 Torr and $k_{298} = 1.98 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, this would lead to a maximum loss-rate of ~5,500 s⁻¹. It is important to note that I find a significant difference between the relative rate of hydroxyacetone compared with the absolute measurements of (Cornwell et al., 2024) (1.98×10^{-13} vs $1.02 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively). My determination is more consistent with what would be expected for alkyl-substituted alcohols or ketones (McGillen et al., 2017; Taatjes et al., 2012; Tadayon et al., 2018), and whereas it would be presumptuous to state that Cornwell et al.'s measurements are in error, I can hypothesize that these lower volatility compounds present additional experimental challenges in flowing systems.

By contrast, the relative rate method was able to provide robust kinetic fits under low-ppb reactant conditions ($\leq 10^{-4}$ of those typically required in absolute measurements). As a result, despite being about three orders of magnitude less reactive than carboxylic acids, alcohols could still be measured reliably with the relative rate method. In my experiments on acids, I observed the formation of masses attributable to α -alkoxyacyl hydroperoxides and its associated anhydride dehydration product. Although the reactions of alcohols are comparatively slower, I was still able to observe the formation of α -alkoxyalkyl hydroperoxides and their corresponding dehydration products, the formates. The detection of these products provides further evidence for the occurrence of CH₂OO insertion reactions. But this method is not only limited to the insertion mechanism, but also is expected to be applicable to other co-reactants that undergo addition or cycloaddition reactions with SCIs.

By employing a near-explicit box model to simulate the reaction system, I was able to reproduce the observed concentration decay and product accumulation trends. Furthermore, by tagging the competitive reactions of other oxidants present in the system (e.g., RO₂, HO₂, RO, and OH), I estimated their relative contributions to the loss of the target compounds. The results indicate that the

contributions of RO₂, RO, and HO₂ are negligible, all below 0.0001%. In contrast, reactions with OH were found to be more significant, but still minor, accounting for up to 4% of the loss in the case of 1-hexanol. This effect is likely attributable to efficient HO_x cycling in the chamber. It is worth noting that the 1-hexanol case represents a worst-case scenario, since its OH rate coefficient is larger than those of the smaller homologues.

This chapter demonstrates the feasibility of the relative rate approach in Criegee kinetics, providing a methodological foundation for further exploration of CI reactivity with complex atmospheric species. Nevertheless, reliable absolute rate coefficients are still required as references to validate and cross-check the relative measurements. Beyond CH₂OO, the applicability of other symmetric alkenes also merits investigation in the future, which will largely depend on the competition between the unimolecular decay of the corresponding SCIs and the target bimolecular reaction rates.

On the basis of the findings in Chapter 3, in Chapter 4 I employed the insertion reactions of SCIs into acids to achieve the *in situ* gas-phase synthesis of α -alkoxyacyl hydroperoxides in an atmospheric simulation chamber. Under excess-ozone conditions, by carefully controlling the absolute concentrations and relative ratios of propene and acid, I was able to effectively generate and detect the target ROOHs, thereby creating a prerequisite for subsequent kinetic experiments. I determined the rate coefficients for two ROOHs—HPMA and HPEA, formed via the insertion of CH₂OO and CH₃CHOO into acetic acid—in their reactions with OH and NO₃. In these experimental systems, the reliability of the derived rate coefficients was highly dependent on constraining the radical budget: the addition of radical scavengers (e.g., cyclohexane), the amount of residual acid, and the large quantities of carbonyls produced during ozonolysis all directly influenced the availability of the target oxidants (OH, NO₃, or CH₂OO). It should be noted that the signals of HPMA and HPEA were strongly perturbed by the concurrent insertion of CH₂OO into isomers of acetic acid, preventing me from reliably deriving bimolecular rate coefficients for their reactions with CH₂OO. In addition, I also determined the rate coefficients for the reactions of NO₃ and CH₂OO with *tert*-butyl hydroperoxide (commercially available) using the relative rate method, together with literature values for OH to provide a benchmark for ROOH reactivity.

The experimental results show that HPMA and HPEA are less reactive toward OH and NO₃ than TBHP, likely due to the strong electron-withdrawing and resonance-inducing effects of the α -alkoxyacyl substituent, which attenuate hydrogen abstraction at the –OOH site. The rate coefficient for the TBHP + CH₂OO reaction is in excellent agreement with previous measurements by (Caravan et al., 2024), where they suggested that these oligomerizations of SCIs could even occur under humid forest regions. By combining these newly obtained kinetic data with simulated photolysis rate and assumed first-order loss by wet deposition, I present an assessment of the atmospheric lifetime for an α -alkoxyacyl hydroperoxide. The results indicate that OH oxidation is the dominant sink, followed in sequence by photolysis, wet deposition, NO₃ oxidation, and Cl oxidation. However, if represented by TBHP, the contribution of NO₃ oxidation would increase significantly, becoming comparable to OH oxidation and one of the most important removal pathways, demonstrating the sensitivity of the NO₃ reaction to inductive substitution effects in peroxidic species. Despite the fact that these oxidation pathways appear to be the dominant gas-phase losses, their rate coefficients are not very high. It is therefore to be expected that for more complex and multifunctional ROOHs, their atmospheric lifetimes are more likely to be controlled by particle-phase uptake and heterogeneous processing, thereby contributing to secondary organic aerosol formation. Notably, Cl oxidation appears negligible under the conditions considered. If the observations of Caravan et al. are valid, ambient [SCI] would need to be at least two orders of magnitude higher than current estimates for this pathway to become competitive with the other sinks. Given the large uncertainties in ambient [SCI], a conclusive answer remains elusive and future exploration in this direction is undoubtedly of great importance.

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Publications and Research activities

Listed below are the papers (published/in preparation), conference attended, and additional research training completed during this PhD program:

Conference presentations:

Pengcheng, W., Abdelwahid, M., Véronique, D., Valéry, C., Max, R. M., (2025) Illuminating the Role of Trifluoroacetaldehyde Photolysis in the Unaccounted Atmospheric Sources of Fluoroform (HFC-23) Emissions. *Workshop on theoretical physical chemistry and atmospheric chemistry, Marseille, France*, <https://atmotheory.github.io/index.html> – Poster

Pengcheng, W., Yue, W., Yangang, R., Jinhe, W., Véronique, D., Abdelwahid, M., Max, R. M., (2024) Gas-phase Kinetics of Criegee Intermediates and their Hydroperoxide products: Expanding the Reactivity Database using a Novel Relative Rate Technique. *Sino-French Joint Workshop on Atmospheric Environment, Bordeaux, France*, <https://sfjw24.sciencesconf.org/> – Oral

Pengcheng, W., Yue, W., Yangang, R., Jinhe, W., Véronique, D., Abdelwahid, M., Max, R. M., (2024) Gas-phase Kinetics of Criegee Intermediates: Expanding the Reactivity Database using a Novel Relative Rate Technique. *27th International Symposium on Gas Kinetics and Related Phenomena, Leeds, UK*, <https://www.rsc.org/events/detail/76465/the-27th-international-symposium-on-gas-kinetics-and-related-phenomena-gk2024-leeds> – Oral

Pengcheng, W., Abdelwahid, M., Véronique, D., Max, R. M., (2024) Gas-phase kinetics of Criegee intermediate reactions with implications for aerosol formation in the atmosphere. *Molecular-Level Understanding of Atmospheric Aerosols, Cargèse, France*, <https://muoaa2024.sciencesconf.org/> – Oral

Pengcheng, W., Abdelwahid, M., Véronique, D., Max, R. M., (2023) Gas Phase Photolysis Kinetics of Trifluoroacetaldehyde: A Comprehensive Investigation of Mechanisms and HFC-23 Yields. *Young Generation Symposium on H₂, Orléans, France*, – the best poster award

External training:

- ACTRIS Intercomparison Campaign for Nitrogen Oxides (NO_x) at Research Centre Jülich (2023) Germany 100h
- Atmospheric and Environmental research infrastructure online training (2023) online 20h
- Innovation in Atmospheric Measurement Techniques: a virtual workshop (2023) online 20h

Publications:

Pengcheng Wang, Yue Wang, Jinhe Wang, Abdelwahid Mellouki, Véronique Daële, Yangang Ren, and Max R. McGillen. 2025. Development of a Relative Rate Technique to Measure Criegee Intermediate Reactivity. *Environmental Science & Technology Letters* 12(7), 842-847.

Rabi Chhantyal-Pun, Pengcheng Wang, Shefali Baweja, Joseph Bainbridge, Chenyang Xue, Véronique Daële, Abdelwahid Mellouki, Max R. McGillen. 2025. Yield of the Four-carbon Stabilized Criegee Intermediates from Isoprene Ozonolysis. *ACS Earth and Space Chemistry*

Pengcheng Wang, Abdelwahid Mellouki, Véronique Daële, Alexandre Kukui, Valéry Catoire, Claude Robert, and Max R. McGillen. 2025. The Potential Contribution of Trifluoroacetaldehyde Photolysis to Unaccounted-for Atmospheric Sources of Controlled Substance HFC-23. – *in prep.*

Pengcheng Wang, Chenyang Xue, Abdelwahid Mellouki, Véronique Daële, Max R. McGillen. 2026. Gas-phase kinetics of Criegee intermediates with a selection of organic acids. – *in prep.*

Pengcheng Wang, Chenyang Xue, Abdelwahid Mellouki, Véronique Daële, Max R. McGillen. 2026. Gas-phase kinetics of Criegee intermediates with a selection of diketones. – *in prep.*

Pengcheng Wang, Chenyang Xue, Abdelwahid Mellouki, Véronique Daële, Max R. McGillen. 2026. Gas-phase kinetics of α -alkoxyacyl hydroperoxides and *tert*-butyl hydroperoxide with OH, NO₃ and Criegee intermediates. – *in prep.*

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Pengcheng WANG

Caractérisation de la réactivité des polluants atmosphériques multigénérationnels en phase gazeuse

Résumé :

Les molécules partiellement oxydées produites au cours des réactions d'oxydation multigénérationnelles représentent un problème central mais encore mal compris en chimie atmosphérique, dont beaucoup sont associées à la formation d'aérosols organiques secondaires ainsi qu'au relargage indirect de gaz à effet de serre puissants. Cette thèse vise à faire progresser notre compréhension de ces processus grâce à des expériences en laboratoire et à des innovations méthodologiques.

Ce travail fournit de nouvelles données cinétiques permettant d'interpréter les conséquences environnementales liées à certaines molécules intermédiaires issues à la fois des émissions anthropiques et biogéniques. La photolyse du trifluoroacétaldéhyde conduisant à la formation de CHF₃ a été caractérisée par des expériences dédiées, ce qui nous a permis d'évaluer le potentiel de réchauffement climatique indirect de ses précurseurs fluorés. Le développement d'une méthode de taux relatif en chambre pour mesurer la cinétique des intermédiaires de Criegee nous a permis d'élargir de manière efficace et fiable la base de données sur ces intermédiaires, tout en nous permettant de synthétiser leurs produits α -alkoxyacyl hydroperoxydes et d'étudier leurs réactions d'oxydation ultérieures. Cela nous permet d'évaluer les durées de vie atmosphériques de ces composés fonctionnalisés et d'estimer leur rôle dans la formation des aérosols organiques secondaires. Cette thèse contribue à replacer la chimie multigénérationnelle dans un contexte environnemental.

Mots clés : Chimie atmosphérique, Cinétique chimique, Oxydation

Characterizing the gas-phase reactivity of multigenerational air pollutants

Summary :

Partially oxidized molecules produced during multigenerational oxidation reactions represent a poorly understood but central issue in atmospheric chemistry, many of which are associated with the formation of secondary organic aerosols and the indirect release of potent greenhouse gases. This thesis aims to advance our understanding of these processes through laboratory experiments and methodological innovation.

This work provides new kinetic data for interpreting the environmental consequences caused by some intermediate molecules arising from both anthropogenic and biogenic emissions. The photolysis of trifluoroacetaldehyde to produce CHF₃ was characterized through dedicated experiments, allowing us to assess the indirect global warming potential of its fluorinated precursors. The development of a chamber-based relative rate method for measuring Criegee intermediate kinetics enabled us to efficiently and reliably expand the Criegee intermediate database, while also allowing us to synthesize their α -alkoxyacyl hydroperoxide products and investigate their subsequent oxidation reactions. This allows us to evaluate atmospheric lifetimes of these functionalized compounds and to estimate their role in secondary organic aerosol formation. This thesis helps to place multigenerational chemistry into an environmental context.

Keywords : Atmospheric chemistry, Chemical kinetics, Oxidation



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