# Criegee Intermediates: What Direct Production and Detection Can Teach Us About Reactions of Carbonyl Oxides

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## Abstract

The carbonyl oxide intermediates in the ozonolysis of alkenes, often known
as Criegee intermediates, are potentially important reactants in Earth's at-
mosphere. For decades, careful analysis of ozonolysis systems was employed
to derive an understanding of the formation and reactions of these species.
Recently it has proved possible to synthesize at least some of these intermedi-
ates separately from ozonolysis, and hence to measure their reaction kinetics
directly. Direct measurements have allowed new or more detailed under-
standing of each type of gas-phase reaction that carbonyl oxides undergo,
often acting as a complement to highly detailed ozonolysis experiments.
Moreover, the use of direct characterization methods to validate increasingly
accurate theoretical investigations can enhance their impact well beyond the
set of specific reactions that have been measured. Reactions that initiate par-
ticles or fuel their growth could be a new frontier for direct measurements
of Criegee intermediate chemistry.

# INTRODUCTION

The reactions of ozone with organic species have been a subject of intellectual and practical interest for well over a hundred years; Carl Harries (1) carried out detailed investigations of ozonolysis at the beginning of the twentieth century. The work of Rudolf Criegee (2, 3) gave us the mechanistic description of ozonolysis that is accepted today (although some ozonolysis reactions do not proceed by the Criegee mechanism; for example, see 4). In particular, Criegee proposed that after $O_3$ adds to the double bond, the initial ozonide divides to form a carbonyl and a carbonyl oxide (**Figure 1**). This latter species is now often referred to as a Criegee intermediate, although, confusingly, this is not the only intermediate named for Criegee (5).

One of the important areas for ozone reactions is in the chemistry of Earth's troposphere (including indoor environments; see 7, 8), where ozone is one of the major oxidants. The fate of carbonyl oxide Criegee intermediates can help determine how hydrocarbon oxidation affects cycles of reactive intermediates such as $NO_x$ and $HO_x$, as well as how aerosol particles form and age. As a consequence, atmospheric chemists have long carried out carefully controlled ozonolysis experiments, combined with detailed calculations, to discover how these elusive intermediates behave. This rich body of research, like the extensive studies of ozonolysis in solution, has given a great deal of information about the mechanism of the reactions that Criegee intermediates undergo (9–12).

Recently it has become possible to synthesize and detect at least some atmospherically important Criegee intermediates in the gas phase and to directly measure their reactions. This review
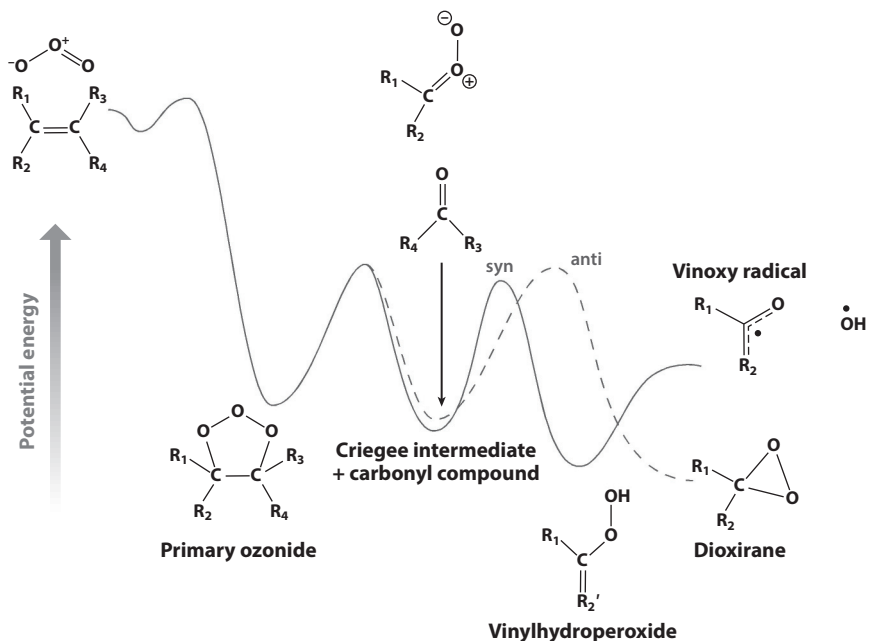


**Figure 1**

A schematic diagram of the energetics of Criegee intermediate formation from ozonolysis and of subsequent unimolecular transformations of the Criegee intermediate. Because of the exothermicity of ozonolysis, Criegee intermediates can be born with enough internal energy to surmount the barriers to dissociation or isomerization. Figure adapted from Reference 6 with permission.

highlights some of the areas in which that new ability has given a more detailed picture of carbonyl oxide reactions. Several reviews and perspectives have appeared very recently (6, 13, 14), and this article does not attempt to review material covered in those works, but rather concentrates on areas with the most recent discoveries and major opportunities.

## OZONOLYSIS MEASUREMENTS AND IMPLICATIONS FOR CRIEGEE INTERMEDIATE CHEMISTRY

The Criegee mechanism for ozonolysis was first verified by liquid-phase experiments, and products of reactions of the carbonyl oxide intermediates have been identified in solution. These observed products are a guide to the probable course of similar reactions in the gas phase. For example, in the Criegee ozonolysis mechanism (2), reaction of carbonyl oxides with carbonyls forms secondary ozonides (1,2,4-trioxolanes), which are also observed in similar reactions in the gas phase (15–17). Because these secondary ozonides are known products of Criegee intermediate reactions, their formation can be used as a marker of Criegee intermediate concentrations in laboratory systems. In one notable set of experiments, Fenske et al. (18) directly studied reactions of thermalized $CH_3CHOO$ Criegee intermediate from 2-butene ozonolysis in a flow tube by reacting the $CH_3CHOO$ with excess acetaldehyde added through a movable injector. In this way, the amount of secondary ozonide product is a reporter for the $CH_3CHOO$ concentration as a function of distance (and hence reaction time) and could be used to make direct measurements of absolute kinetics for $CH_3CHOO$ decomposition and reaction with acetaldehyde (18).

The correlation between solution-phase results and gas-phase ozonolysis is complicated by the fact that, in the gas phase, not all Criegee intermediates are stabilized before unimolecular or bimolecular reactions (12). This is in fact a substantial added difficulty; Horie & Moortgat (10, p. 387) called the presence of excited and dissociating Criegee intermediates "the source of all the problems which studies on the gas-phase ozonolysis must suffer." Moreover, beyond the formation of excited Criegee intermediates, the reactions of even thermalized Criegee intermediates can form energetic products that are stabilized in solution but dissociate in the gas phase. Despite this complexity, carefully controlled ozonolysis experiments have been able to deduce critical parameters, especially about the relative rate coefficients of Criegee intermediate reactions with different species.

Nevertheless, a requirement for accurate chemical models of the atmosphere is the availability of reliable absolute rate coefficients, which for the case of Criegee intermediate reactions had been subject to substantial uncertainty before the ability to directly produce and measure carbonyl oxides. Bridging this knowledge gap is increasingly a role for theory and computation, in conjunction with direct experimental measurements. Advances in quantum chemistry and modern statistical kinetics theory have pushed the best theory to a level of accuracy approaching or bettering even careful experiments (19, 20). The ability to compare high-level theory and direct experimental measurements on isolated elementary reactions of Criegee intermediates can dramatically extend the scope of our knowledge of carbonyl oxide reactivity.

## DIRECT PRODUCTION AND DETECTION OF CRIEGEE INTERMEDIATES

The direct detection of carbonyl oxides in the gas phase has been a longstanding goal for ozonolysis research. In solution and in matrix, some particularly stable carbonyl oxides were isolated and characterized beginning in the 1980s, as reviewed by Sander (21). The challenge for direct measurement of Criegee intermediate reactions, in solution or in the gas phase, is that ozonolysis

is relatively slow, and subsequent reactions of the carbonyl oxides can be rapid. Hence, not only is it necessary to have a sensitive and selective means to detect the Criegee intermediates, but it is also necessary to have a way to make enough of them that their reactions can be studied directly. This requirement implies a need for nonozonolysis synthetic methods (22). In early experiments on isolating carbonyl oxides in solution or in matrix, two main methods were successful (21, 23): combination of triplet carbenes with $O_2$ and reaction of singlet $O_2$ with diazo compounds. In both cases, the substantial exothermicity of the reactions is carried away by the efficient thermalization in the condensed-phase environment. In fact, by employing matrix codeposition of ozone and alkenes, Ault and coworkers (24, 25) have succeeded in detecting carbonyl oxides directly from ozonolysis. However, for producing and measuring Criegee intermediates in the gas phase, a less energetic reaction is required.

The first gas-phase detection of carbonyl oxides was built on theoretical predictions that formaldehyde oxide, $CH_2OO$, could be produced from dimethyl ether (DME) (26) or dimethyl sulfoxide (DMSO) (27) oxidations. In the DMSO oxidation, the reaction of $CH_3S(=O)CH_2$ radical with $O_2$ produces $CH_2OO$ and a $CH_3SO$ radical. This reaction is slightly exothermic [by 12.5 kcal/mol at the CBS-QB3 level (27)], and even at low pressure and room temperature, enough $CH_2OO$ could be produced to be detected by tunable synchrotron photoionization mass spectrometry (28). Later, an improved synthetic method based on the reactions of $CH_2I$ radicals with $O_2$ (29) was able to form enough $CH_2OO$ radicals to carry out kinetics investigations (30). This reaction has since been characterized in some detail (31, 32). Moreover, similar reactions of other *gem*-iodoalkyl radicals have been shown to produce corresponding carbonyl oxide Criegee intermediates: $CH_3CHOO$ (33–35), $(CH_3)_2COO$ (31, 36), and $CH_3CH_2CHOO$ (37).

Detection of gas-phase Criegee intermediates has been successfully implemented by photoionization spectroscopy (28, 30, 35, 38, 39), ultraviolet spectroscopy (31, 33, 34, 36, 37, 40–47), infrared spectroscopy (31, 48–51), and rotational spectroscopy (52–60). Indeed, Ahrens et al. (50) attributed infrared features to Criegee intermediates in their Fourier-transform infrared (FTIR) study of β-pinene ozonolysis, and Womack et al. (52) used rotational spectroscopy to identify $CH_2OO$ from the ozonolysis of ethene, despite the formidable challenges of detecting Criegee intermediates in ozonolysis, as described above. The experimental characterization of the structure and bonding in the carbonyl oxides themselves has helped to confirm the dominant configuration of the isolated gas-phase Criegee intermediate species as zwitterions (14). The reactivity of Criegee intermediates may seem somewhat unusual, as the dominant electronic configuration of the carbonyl oxide is a closed-shell singlet, $H_2C = O^{\delta+}O^{\delta-}$. Recently it has been proposed that some of the reactivity of the Criegee intermediates arises from mixing of the zwitterionic ground state with the first triplet state (a nearly pure biradical state) upon bond formation (61). This review concentrates on how the ability to isolate carbonyl oxides has led to discoveries about the reactions of these species.

## IMPORTANT REACTIONS OF CRIEGEE INTERMEDIATES

In solution-phase ozonolysis, the important classes of reactions of the carbonyl oxides were summarized by Criegee (2) as dimerization, reactions with carbonyls, isomerizations, and reactions with "proton-active substances." In the context of gas-phase and atmospheric chemistry, these classes can be generalized as association with other 1,3-bipoles, cycloaddition reactions, unimolecular reactions, and insertion reactions. The list can be extended by consideration of one further class: addition to radical species (14). The advent of direct synthesis and detection methods has enabled new discoveries and new opportunities related to all five classes of reactions.

## Reaction with 1,3-Bipoles: Self-Reaction of Carbonyl Oxides

Rapid self-reactions of carbonyl oxides had been well known in solution-phase ozonolysis, and the identification of dimers and mixed dimers was one of the pieces of evidence for the Criegee mechanism. In the gas phase, direct measurements of the self-reaction of formaldehyde oxide showed a nearly collision-limited rate coefficient (46, 49, 62, 63), consistent with a barrierless association as calculated by Vereecken et al. (64). The association forms a relatively rigid cyclic 1,2,4,5-tetroxane complex from head-to-tail cycloaddition, with exothermicity of about 100 kcal/mol; the excess energy allows many possible rearrangements and dissociations (64), but no gas-phase product studies are yet available.

## Cycloaddition Reactions

**Reactions with carbonyls and alkenes.** The reaction of carbonyl oxides with carbonyl compounds is a key step in the Criegee mechanism of ozonolysis. In the gas phase, as in the liquid phase, these reactions are cycloadditions to the $C=O$ bond, and form 1,2,4-trioxolane "secondary ozonides" (65), which have been detected from gas-phase reactions (16) and used to assay carbonyl oxide concentrations for kinetics measurements (18). Jalan et al. (65) predicted that, at low pressure, the chemically activated trioxolane from reactions of $CH_2OO$ with carbonyls could isomerize and dissociate to other products, for example to regenerate the carbonyl compound and produce formic acid, the organic acid isomer of the Criegee intermediate, in what is effectively a carbonyl-assisted tautomerization.

Direct detection of Criegee intermediates has allowed absolute rate coefficient measurements for their reactions with ketones and aldehydes (38, 66–68); in general these rate coefficients are in qualitative agreement with measurements that employed ozonolysis and indirect detection (14). For example, the reaction of $CH_2OO$ with $CH_3CHO$ was measured as $(1.48 \pm 0.04) \times 10^{-12}$ cm$^3$/s by photolytic production of $CH_2OO$ but indirect detection of $CH_2OO$ via $CH_2O$ (68); as $(9.5 \pm 0.7) \times 10^{-13}$ cm$^3$/s by direct photoionization detection of $CH_2OO$ (38); as $(1.1 \pm 0.1) \times 10^{-12}$ cm$^3$/s by direct ultraviolet detection of $CH_2OO$ (67); and as $(1.7 \pm 0.5) \times 10^{-12}$ cm$^3$/s from ozonolysis (69). The small discrepancies among these values may simply reflect the weak pressure dependence of the reaction (67).

Cycloaddition reactions are some of the few reactions of Criegee intermediates for which temperature dependence has been measured, by the Green group at MIT. Buras et al. (66) measured the kinetics of cycloadditions of $CH_2OO$ with several alkenes, finding a weak positive activation energy and rate coefficients at 298 K for all of the alkenes around $10^{-15}$ cm$^3$/s, i.e., much smaller than cycloadditions of $CH_2OO$ with carbonyls. In contrast, the recent measurements by Elsamra et al. (67) showed a negative temperature dependence of the reactions of $CH_2OO$ with acetone and acetaldehyde. They also carried out transition state theory and master equation calculations that showed reasonable agreement with the experimental observations. Extension of their calculations to high temperature showed that the rate coefficients for cycloaddition to carbonyls and to alkenes converged, implying that the differences in rate coefficients at lower temperature are dominated by energetic factors.

**Reaction with SO$_2$.** Of the results from direct Criegee intermediate detection, the observation that carbonyl oxides react rapidly with SO$_2$ has probably drawn the most immediate attention. The potential for Criegee intermediates to contribute to sulfate production had been recognized at least since the work of Cox & Penkett in 1971 (70, 71), but determinations based on changes in OH formation upon SO$_2$ addition to ozonolysis systems appeared to imply relatively low rate

coefficients (72, 73). The direct measurements of Welz et al. (30) showed that the simplest Criegee intermediate, $CH_2OO$, reacted with $SO_2$ with a rate coefficient of $(3.9 \pm 0.7) \times 10^{-11}$ cm³/s, many orders of magnitude above the rate coefficients used in atmospheric models.

Reaction of $SO_2$ with a carbonyl oxide is initiated by cycloaddition of the C–O–O carbonyl oxide group across one of the S=O bonds in $SO_2$ (9, 74, 75) to form a heteroozonide with a secondary ozonide structure. How this heteroozonide is eventually converted in ozonolysis experiments to $SO_3$ or $H_2SO_4$ and a carbonyl has not yet been completely characterized. Ozonolysis experiments that considered the dependence of formic acid and $H_2SO_4$ yields on total pressure and on the concentration of added $SO_2$ (9) suggested that the adduct reacts with $SO_2$, and Martinez & Herron (76) inferred a reaction of the adduct with $H_2O$. Direct low-pressure photoionization experiments (30, 35) measured $SO_3$ formation on the same timescale as Criegee intermediate disappearance, which could indicate rapid dissociation of the chemically activated adduct. Recently, Kuwata et al. (77) carried out an extensive theoretical reinvestigation of Criegee intermediate reactions with $SO_2$. They showed that transition states leading from the heteroozonide to $CH_2O$ and $SO_3$ lie well below the energy of the $CH_2OO + SO_2$ reactants, and below transition states leading to the $SO_2$-assisted isomerization product HCOOH. They found similar results for the reaction of $(CH_3)_2COO$ with $SO_2$. They also calculated that very little of the heteroozonide should be stabilized and predicted near-unity yields of $SO_3$ for both reactions at atmospheric pressure, a conclusion that differs from earlier calculations (78).

A rapid reaction of Criegee intermediates with $SO_2$ would likely have become evident even without direct detection, although the absolute magnitude of the rate coefficient may have been deduced more slowly. Mauldin et al. (79) measured OH and $H_2SO_4$ in a forest site in Hyytiälä, Finland, and showed definitively that some non-OH tropospheric oxidant of $SO_2$ had a substantial effect on $H_2SO_4$ formation above boreal forests. They combined that insight with laboratory experiments showing that some product of terpene ozonolysis was this oxidant. Both field measurements and laboratory experiments determined [OH] by converting it to isotopically labeled sulfuric acid by reaction with $^{34}SO_2$. **Figure 2** shows a key figure from that paper. Mauldin et al. were able to correct for reactions of OH by employing an OH scavenger, and noted a substantial residual production of $H_2SO_4$ from $SO_2$ oxidation by some unknown oxidant. Because of the titration they were able to deduce the atmospheric concentration of the oxidant ($\sim 10^6$ cm$^{-3}$). The modeled $H_2SO_4$ concentration, including only the previously known oxidation reactions of $SO_2$, is systematically lower than the measurements, as shown in **Figure 2**. In their laboratory experiments, Mauldin et al. (79) measured $H_2SO_4$ formation from addition of $SO_2$ to ozonolysis of limonene or α-pinene, as well as to ozonolysis of direct emissions from tree branches, and demonstrated that a non-OH oxidant was present in these systems. They postulated that this species, which they denoted by X, was a stabilized Criegee intermediate. Using their estimated rate coefficients for reactions of $SO_2$ with species X from ozonolysis of limonene ($8 \times 10^{-13}$ cm³/s) or α-pinene ($6 \times 10^{-13}$ cm³/s) and the deduced concentration of species X, they were able to successfully model the field measurements, as shown in **Figure 2**. Note that their rate coefficients are smaller than the directly measured rate coefficients for reactions of Criegee intermediates with $SO_2$.

Subsequent ozonolysis work of Berndt et al. (80) also suggested a smaller rate coefficient than the direct measurements (30), but still substantially larger than previous tropospheric chemistry models had employed. Significantly, Berndt et al. (81) later pointed out that the ozonolysis measurements determined relative rate coefficients, and that the ratios of rate coefficients that had been directly measured were in reasonable agreement with similar determinations from ozonolysis. Also, the theoretical investigations had begun to converge on the correct description well before direct experimental investigations were possible. The earlier theory from Kurtén et al. (75) showed that there was no fundamental reason that the reactions should not be very rapid.
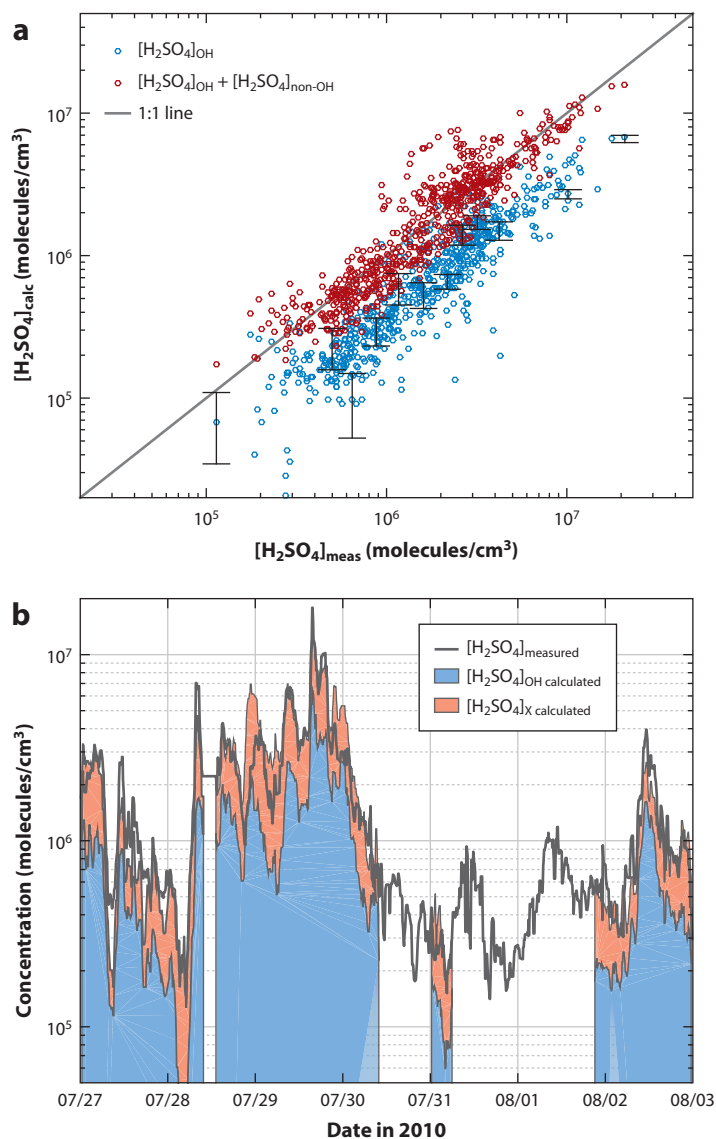
**Figure 2**

Measured and modeled sulfuric acid concentrations at a boreal forest field station in Hyytiälä, Finland.
(*a*) The model with the previously known OH-initiated oxidation of $SO_2$ (*blue symbols*) is unable to account
for the observed $H_2SO_4$, leading to the deduction that a non-OH oxidant (species X) must contribute to
sulfuric acid production. Ozonolysis experiments determined an effective rate coefficient for reaction of
species X, presumed to be a stabilized Criegee intermediate, with $SO_2$. Including that reaction (*red symbols*)
brings the model into closer agreement. (*b*) A time sequence of the measurements throughout the campaign,
showing the substantial contribution of oxidation by species X (*red shaded area*) to the total $H_2SO_4$
concentration (*black line*). The contribution from OH-initiated oxidation of $SO_2$ is shown as the blue shaded
area. Figure adapted from Reference 79 with permission from Macmillan Publishers Ltd.

The initial direct measurements of Criegee intermediate reactions with $SO_2$ were followed by many measurements that confirmed the initial result (41, 63, 68, 82). The reaction of $CH_2OO$ with $SO_2$ has a negligible change in rate coefficient as a function of pressure (63). Direct determinations have also demonstrated rapid reaction of larger Criegee intermediate species with $SO_2$; Taatjes et al. (35) and Sheps et al. (34) measured large rate coefficients for the reactions of *syn*-$CH_3CHOO$ and *anti*-$CH_3CHOO$ with $SO_2$. Both studies showed a larger rate coefficient for the *anti* conformer; the UV absorption experiments of Sheps et al. (34) implied a stronger conformer dependence than the photoionization measurements of Taatjes et al. (35), which may reflect better conformer selectivity of the ultraviolet detection method. Finally, the recent measurements of Huang et al. (31) demonstrate that the doubly methyl substituted carbonyl oxide, $(CH_3)_2COO$, reacts even more rapidly with $SO_2$. They also noted a pressure dependence of this reaction, suggesting that the stabilization of the addition complex may be kinetically important.

The reaction of Criegee intermediates with $SO_2$ drew attention not only because of the substantial difference between the directly measured rate coefficient and previous measurements, but because of the potential tropospheric implications for sulfate aerosol formation (79). In fact, there appear to be uniformly large rate coefficients for Criegee intermediates with $SO_2$, as discussed above; but an important question is what the concentration of Criegee intermediates in the troposphere is likely to be (83). The prediction of the tropospheric concentration of carbonyl oxides depends on knowing their production and removal rates, both of which are subject to considerable uncertainty. Criegee intermediates are formed in ozonolysis of alkenes, but the inventory of alkenes remains incomplete and uncertain (84, 85). The fraction of ozonolysis that produces Criegee intermediates and the nature of the Criegee intermediates that are formed both depend on the particular alkene and the collisional stabilization process (12, 73, 86–89). The removal of Criegee intermediates from the troposphere is often dominated by their unimolecular decomposition and their reaction with water (19, 64, 78).

## Unimolecular Reactions

The unimolecular isomerization and dissociation pathways of carbonyl oxides can form OH radicals, making them important for $HO_x$ cycles in the troposphere. For some Criegee intermediates, the thermal unimolecular decomposition may be a substantial loss mechanism and may therefore affect the Criegee intermediate concentration. Moreover, the isomerization or decomposition of the initially excited carbonyl oxide from hydrocarbon ozonolysis is critical for determining how much stabilized Criegee intermediate is initially formed (12, 86).

The mechanism for isomerization of carbonyl oxides depends substantially on the level of substitution and on the conformer. Isomerization by hydrogen transfer from a C–H bond adjacent to the carbonyl group (e.g., the methyl group in *syn*-$CH_3CHOO$) can lead to a vinyl hydroperoxide (VHP) that is believed to be a precursor to OH production. Isomerization of carbonyl oxides without an available hydrogen atom for VHP formation (e.g., *anti*-$CH_3CHOO$ or $CH_2OO$) is calculated to proceed via C−O−O ring closure to form a dioxirane (see **Figure 1**). The isomerization to a dioxirane has still had essentially no direct experimental measurement, although it is the only unimolecular pathway available to the simplest and most commonly studied Criegee intermediate, $CH_2OO$. This is largely because the isomerization is too slow to be easily disentangled from competing experimental removal processes such as bimolecular or heterogeneous reactions (63). The lowest experimental value for the unimolecular decomposition of $CH_2OO$ using direct detection of the Criegee intermediate is $11 \pm 8 \text{ s}^{-1}$ from Chhantyal-Pun et al. (63), which is an upper limit because it may still contain contributions of diffusion or other loss mechanisms.

For this reaction, however, indirect experiments, informed by the absolute rate coefficients from direct measurements of carbonyl oxide reactions, can do substantially better. Newland et al. (91) derived a negative value, $(-2.3 \pm 3.5) \times 10^{-11}$ cm$^{-3}$, for the ratio of $CH_2OO$ decomposition to its reaction with $SO_2$. Their uncertainty bounds imply an upper limit for decomposition of 4.6 s$^{-1}$ when combined with the absolute rate coefficient (30) for the $CH_2OO$ reaction with $SO_2$. Most recently, Berndt et al. (69) carried out carefully controlled ethene ozonolysis experiments that measured the time-dependent sulfuric acid concentration after titration of $CH_2OO$ with $SO_2$ in an apparatus designed to minimize wall effects, and were able to derive a still lower rate coefficient for the thermal decomposition of $CH_2OO$: $0.19 \pm 0.07$ s$^{-1}$. Although absolute values for carbonyl oxide reactions may have helped justify the choice of experimental conditions to isolate the unimolecular decomposition (69), their final rate coefficient determination is independent of them. Berndt et al. also carried out Rice–Ramsperger–Kassel–Marcus (RRKM) theory calculations using stationary points characterized at the CCSD(T)/aug-cc-pVTZ level and refined by the CHEAT1 (92) extrapolation protocol, which gave a high-pressure limiting rate coefficient value of 0.25 s$^{-1}$, similar to the much earlier prediction by Olzmann et al. (93) of $\sim$0.3 s$^{-1}$, but larger than the CCSD(T)/6-31G(d) transition state theory of Zhang & Zhang (94) or the molecular dynamics calculations of Kalinowski et al. (95). However, because their master equation calculations showed that the decomposition should be in the fall-off region at 1 atm, Berndt et al. postulated that the comparison to experiment may suggest a lower barrier height than their calculations (69). Note that the highest-level [HEAT-345(Q) protocol] calculated barrier height for isomerization from Nguyen et al. (54) is slightly higher (19.1 kcal/mol) than the 18.9 kcal/mol calculated by Berndt et al. (69).

Because the OH radical can be readily and sensitively detected, unimolecular pathways that produce OH are experimentally more accessible. The Lester group (33, 37, 40) has exploited sensitive laser-induced fluorescence (LIF) detection to analyze the absorption spectrum of Criegee intermediates by detecting the OH radical after UV excitation. They also directly measured OH from the decomposition of ground state carbonyl oxides, either from species that retain energy from their formation (96) or after infrared excitation to specific internal energies (90, 97–99). This latter strategy provides an exquisite probe of the energy-dependent rates for production of OH from Criegee intermediate dissociation. Liu et al. detected OH production as a function of excitation in the CH overtone region of *syn*-$CH_3CHOO$ (97) and $(CH_3)_2COO$ (98), and employed detailed theory that not only identified the specific vibrational motions of the resulting IR action spectrum, but also showed how these motions coupled to the intrinsic reaction coordinates that lead to the dissociation to form OH. These results led to an even more remarkable achievement, as the timescale for production of OH was resolved from excitation near the barrier to dissociation (90). This is in essence a determination of the microcanonical rate coefficients for the unimolecular reaction in this region of energy; the results are shown in **Figure 3**. Moreover, these experiments could be directly compared to statistical RRKM theory calculations based on high-level quantum chemistry characterization of the carbonyl oxides, the vinyl hydroperoxide isomeric intermediates, and the transition state barriers. As can be seen in **Figure 3**, the agreement between the first-principles theory and the experiment is stunning. The detailed electronic structure theory also allows accurate statistical master equation calculations of the thermal isomerization rate coefficient, giving what are probably the best estimates of the purely thermal unimolecular loss of *syn*-carbonyl oxides: The measurements of Fenske et al. (18) returned a decomposition rate for $CH_3CHOO$, 76 s$^{-1}$, smaller than the RRKM master equation calculations, but whose factor-of-three uncertainty limits easily encompass the theoretical value of 166 s$^{-1}$. In fact, later direct measurements by Smith et al. (45) of the thermally averaged rate coefficients for $(CH_3)_2COO$ decomposition are in excellent agreement with both the master equation values of Fang et al. (90) and their own calculations.
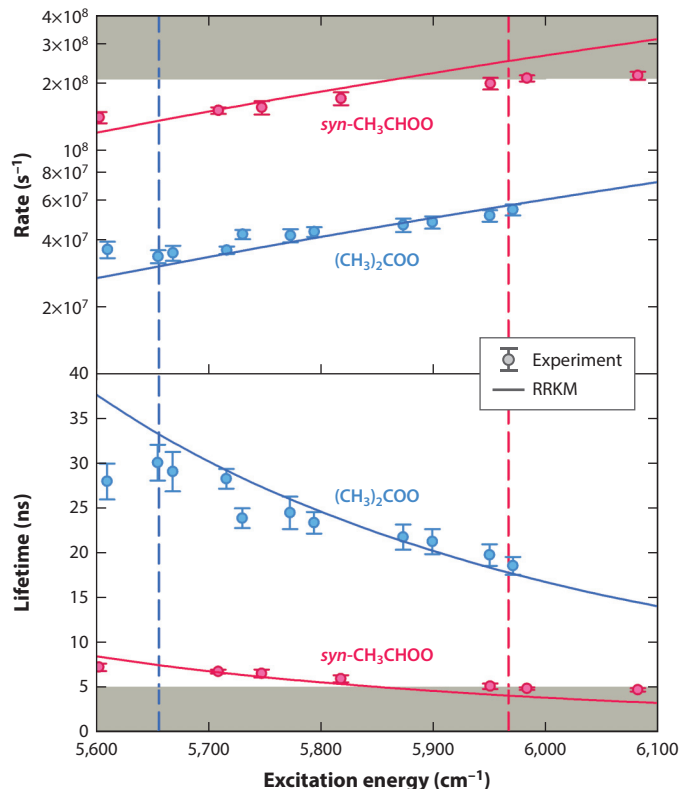
**Figure 3**

Direct measurements and RRKM (Rice–Ramsperger–Kassel–Marcus) calculations of the energy-resolved rate coefficients for dissociation of acetone oxide and acetaldehyde oxide. The Criegee intermediates are excited by an infrared laser to a particular energy level and the time dependence of the OH formation is measured. The RRKM calculations are based on high-level ab initio characterizations of the relevant stationary points. Figure adapted from Reference 90 with permission from AIP Publishing.

The unimolecular decomposition of acetone oxide is a case in which dynamics, kinetics, and theory have all converged on a similar answer, although even in this case some minor discrepancies remain. The ratio of the absolute rate coefficient for $(CH_3)_2COO$ decomposition to that of the reaction with $SO_2$ (45) is smaller than the ratio reported from ozonolysis experiments by Berndt et al. (100) and Newland et al. (91), so that the ozonolysis experiments would tend to suggest larger rate coefficients for decomposition or smaller rate coefficients for reaction with $SO_2$. By contrast, earlier experimental estimates of the unimolecular decay rate coefficients of $(CH_3)_2COO$ from $SO_2$ scavenging experiments (80) and from time-dependent OH yields in ozonolysis (including master equation analysis that allows the separation of contributions from excited and thermal decomposition) (101) appear to imply a far smaller decomposition rate coefficient. Smith et al. (45) suggested that the differences may reflect a stabilization into the vinyl hydroperoxide intermediate well, or simply the difficulties of deriving elementary rate coefficients from the complex process of ozonolysis.

The time-dependent master equation analysis of Kroll et al. (101) began to parameterize and describe the interactions among the exothermic ozonolysis process, the collisional relaxation and dissociation of chemically activated products, and thermal reactions. Zhang & Zhang (94)

calculated stationary points for all the relevant pathways in isoprene ozonolysis and carried out master equation calculations to predict OH yields. Kuwata and coworkers (102) used CBS-QB3 quantum chemistry and RRKM master equation calculations to predict kinetics of the methyl vinyl carbonyl oxides in isoprene ozonolysis. More and more rigorous descriptions of ozonolysis in terms of elementary chemical reactions and collisional energy transfer are becoming feasible, especially as theoretical kinetics methods advance (20, 54). Recently, in a thorough investigation using accurate high-level quantum chemistry and two-dimensional master equation methods, Nguyen et al. (54) calculated the branching ratios for stabilization and decomposition products in ethene ozonolysis.

## Insertion Reactions

The products of reactions of carbonyl oxides with species such as alcohols and hydroperoxides in solution-phase ozonolysis can be viewed as an effective insertion of the carbonyl oxide into the O–H bond. For example, ozonolysis in methanol forms methoxyhydroperoxides (103), a result that gave early support to the view of carbonyl oxides as zwitterions rather than biradicals (2) (**Figure 4**).

In gas-phase ozonolysis, similar reaction products are observed (10). For example, Neeb et al. (104) added formic acid, acetic acid, and methanol to ethene ozonolysis and observed in each case products from insertion of the $CH_2OO$ Criegee intermediate into the RO–H bond. Similarly, Horie et al. (105) identified hydroxymethyl hydroperoxide (HMHP), the product of insertion of $CH_2OO$ into HO–H, when ethene ozonolysis is carried out in the presence of water, similar to observations by Gäb et al. for ozonolysis of hydrocarbons in water (106) and in humid air (107).

In the gas phase, these reactions are initiated by association of the carbonyl oxide with the RO–H reactant in a hydrogen-bonded complex and by subsequent rearrangement of this complex to form the final products. In some cases, other rearrangements may be possible. Kumar et al. (108) showed that water and organic acids could both catalyze isomerization of *syn*-carbonyl oxides to the corresponding vinyl hydroperoxides. Anglada & Solé (109) carried out recent calculations on similar pathways for water monomers and dimers. Vereecken et al. (110) calculated that the hydrogen-bonded complex in reactions of carbonyl oxides with hydroperoxides could form an alcohol oxide or ether oxide intermediate. The alcohol oxide from the reaction of $CH_2OO$ with HOOH is unstable, with only a $\leq 5$ kcal/mol barrier to reform the hydrogen-bonded complex, but the ether oxides are somewhat more stable and could conceivably be isolated. Vereecken et al. (110) predicted rate coefficients for $CH_2OO$ reactions with hydrogen peroxide $(3 \times 10^{-13}$ cm³/s$)$ and methyl hydroperoxide $(6 \times 10^{-12}$ cm³/s$)$ and initial ether oxide yields of up to 85%.
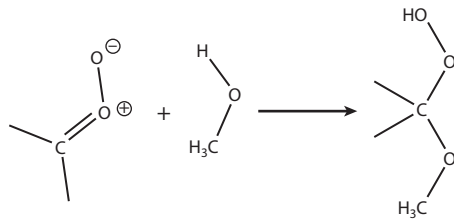


**Figure 4**

Depiction of an insertion reaction of a carbonyl oxide with methanol.

**Reactions with water.** Because of the substantial amount of water in Earth's atmosphere, the reactions of Criegee intermediates with water are crucial parameters in determining their atmospheric concentrations (20, 83). The Criegee intermediate reactions with water traverse a barrier between the hydrogen-bonded initial adduct and the eventual hydroxyalkyl hydroperoxide product, and this barrier's height (and therefore the rate coefficient) has a substantial dependence on the nature and conformation of the carbonyl oxide.

Before the availability of direct synthesis and detection of gas-phase Criegee intermediates, the calculations of reaction rate coefficients for reactions of carbonyl oxides with water varied substantially in absolute magnitude, but agreed in predicting that reactions of Criegee species with alkyl groups in an *anti* configuration to the C–O–O group should have markedly higher rate coefficients than *syn*-carbonyl oxides. Anglada et al. (111) calculated a rate coefficient for *syn*-$CH_3CHOO$ reacting with water as $4.2 \times 10^{-20}$ $cm^3/s$, and for *anti*-$CH_3CHOO$ as $2.5 \times 10^{-15}$ $cm^3/s$; Ryzhkov & Ariya (112) calculated rate coefficients about a factor of three lower ($1.2 \times 10^{-20}$ $cm^3/s$ for reaction of *syn*-$CH_3CHOO$ and $6.7 \times 10^{-16}$ $cm^3/s$ for reaction of *anti*-$CH_3CHOO$); and Kuwata et al. (113) calculated coefficients slightly smaller still ($7.2 \times 10^{-21}$ $cm^3/s$ for reaction of *syn*-$CH_3CHOO$ and $2.9 \times 10^{-16}$ $cm^3/s$ for reaction of *anti*-$CH_3CHOO$). Later, higher-level calculations by Anglada et al. (114) predicted larger rate coefficients and a greater conformer dependence: $2.4 \times 10^{-18}$ $cm^3/s$ for reaction of *syn*-$CH_3CHOO$ and $1.7 \times 10^{-13}$ $cm^3/s$ for reaction of *anti*-$CH_3CHOO$.

Direct detection of $CH_3CHOO$ by synchrotron photoionization mass spectrometry (35), ultraviolet spectroscopy (34), or infrared spectroscopy (51) allows conformer-specific measurements of the Criegee intermediate reactivity. The photoionization experiments of Taatjes et al. (35) observed the preferential removal of *anti*-$CH_3CHOO$ by water and measured a rate coefficient of $(1 \pm 0.4) \times 10^{-14}$ $cm^3/s$ for the reaction. The ultraviolet absorption measurements from Sheps et al. (34) provide a larger value, $(2.4 \pm 0.4) \times 10^{-14}$ $cm^3/s$, which is likely more reliable because of better separation of conformers in the ultraviolet detection (14). In both experiments, the reaction of the *syn*-$CH_3CHOO$ with water was too slow to measure. The latest calculations of Anglada & Solé (109) calculate the rate coefficient for *anti*-$CH_3CHOO$ reacting with water to be $2.4 \times 10^{-13}$ $cm^3/s$, about a factor of ten larger than the measured value.

The calculations of Anglada & Solé (109) also predict that reactions with the water dimer should be far more facile than reactions with a single water molecule for all the Criegee intermediates they investigated. This conclusion matches the earlier work of Ryzhkov & Ariya (112), who predicted that water dimer reactions should be some $10^5$ times more efficient than water monomer reactions in removing Criegee intermediates.

For the reaction of $CH_2OO$ with water, the prediction of rapid reaction with the water dimer has been directly tested. The ethene ozonolysis experiments of Berndt et al. (81) investigated the dependence of sulfuric acid production on water concentration and implied that the reaction of $CH_2OO$ with the water dimer had 0.29 times the rate coefficient of its reaction with $SO_2$, or on the order of $1 \times 10^{-11}$ $cm^3/s$ when combined with the absolute rate coefficient measurements of Welz et al. (30). Chao et al. (115) used ultraviolet absorption spectroscopy to follow directly the decay of $CH_2OO$ produced from photolysis of diiodomethane/$O_2$ mixtures in the presence of varying concentrations of water. As shown in **Figure 5**, they determined a quadratic dependence of the pseudofirst-order removal rate coefficient on water concentration, a clear marker for reaction with the water dimer. The rate coefficient they derived for the dimer reaction, $(6.5 \pm 0.8) \times 10^{-12}$ $cm^3/s$, is in reasonable agreement with the measurements of Berndt et al. (81) and is nearer to the calculated value of Ryzhkov & Ariya (112), $2.7 \times 10^{-12}$ $cm^3/s$, than to the recent calculations of Anglada & Solé (109), which gave a rate coefficient of $2.3 \times 10^{-10}$ $cm^3/s$. As described below, Lin et al. (116) calculated rate coefficients that fall between those of the Ariya group and the Anglada group and that are in reasonable agreement with experiment. The experimental rate
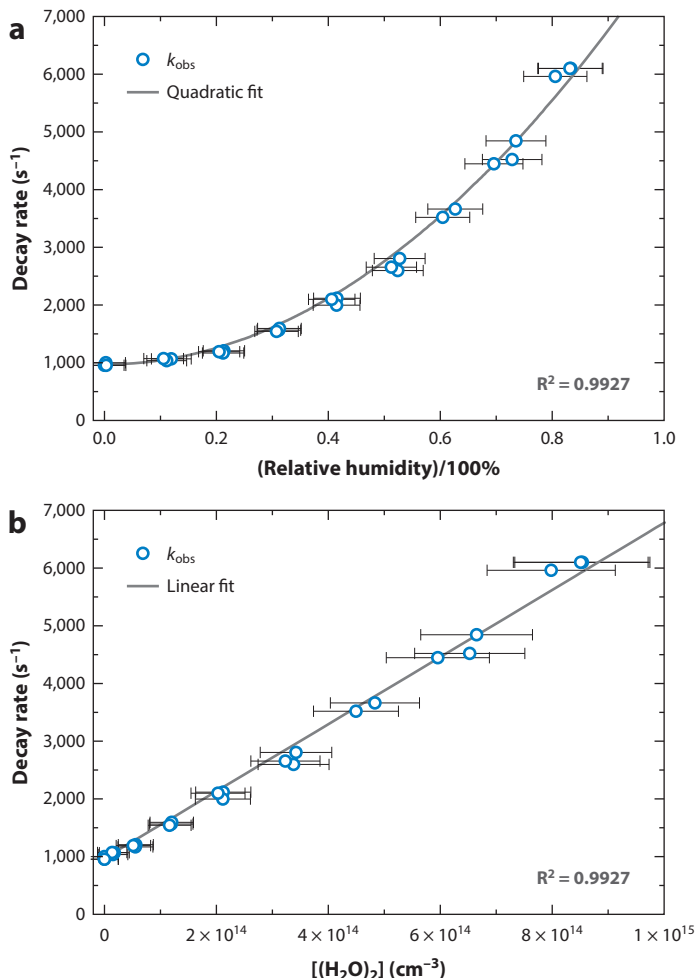
**Figure 5**

(*a*) Directly measured pseudofirst-order decay rate coefficient of $CH_2OO$ as a function of the concentration of water vapor added to the system. The quadratic dependence indicates a substantial role for reactions of the water dimer. (*b*) The same pseudofirst-order rate coefficients, now plotted as a function of the water dimer concentration. The slope of the plot gives the second-order rate coefficient for reaction of $CH_2OO$ with $(H_2O)_2$. Figure adapted from Reference 115 with permission from AAAS.

coefficient has been corroborated by the measurements of Lewis et al. (117), who also employed direct ultraviolet monitoring of photolytically produced $CH_2OO$ and deduced a rate coefficient of $(4.0 \pm 1.2) \times 10^{-12}$ $cm^3/s$.

The direct measurement of a substantial rate coefficient for reaction of the water dimer with $CH_2OO$ confirms the analysis of Vereecken et al. (78) that removal of the simplest carbonyl oxide in the troposphere will be dominated by the water dimer reaction. Recently, Smith et al. (44) carried out an illuminating extension of the work of Chao et al. (115) by measuring the temperature dependence of the $CH_2OO$ reaction with the water dimer. They observed a substantial negative temperature dependence, with an Arrhenius activation energy of $(-8.1 \pm 0.6)$ kcal/mol. This negative activation energy reflects the significant role of the strong hydrogen-bonded

entrance channel complex in determining the rate coefficient of the reaction. Transition state theory calculations using QCISD(T) energies and B3LYP/6-311+G(2d,2p) geometries matched the negative activation energy but underpredicted the magnitude of the rate coefficient by about a factor of three. Lin et al. (116) extended the temperature range of the $CH_2OO + (H_2O)_2$ measurements to higher temperature and performed transition state theory kinetics calculations of rate coefficients for $CH_2OO$ and $CH_3CHOO$ reactions with the water monomer and dimer, based on QCISD(T)/CBS//B3LYP/6-311+G(2d,2p) characterization of the relevant stationary points. Their calculations are in relatively good agreement with the available experimental results for the reactions. Not only does this work (44, 116) corroborate the mechanism of the Criegee intermediate reaction with the water dimer, but the strong temperature dependence will also allow more precise prediction of regional variations in tropospheric $CH_2OO$ removal rates.

Ozonolysis of many terminal alkenes will produce $CH_2OO$, and as the reaction with the water dimer is its dominant removal mechanism, knowing the products of this reaction will be crucial in determining the tropospheric impact of $CH_2OO$. Ozonolysis studies by Neeb et al. (118) reported that HMHP, the insertion product, was the sole product of $CH_2OO$ reaction with 16,000 ppmv of water, and attributed observations of formic acid to heterogeneous reaction of the HMHP. Product analysis of isoprene ozonolysis by Nguyen et al. (119) suggests that the reaction of $CH_2OO$ with the water dimer could produce substantial formic acid (54% yield) at atmospheric conditions. In their measurements, Nguyen et al. calibrated the response of their instrument in order to account for possible heterogeneous removal of products. Their results support the prediction by Ryzhkov & Ariya (112) that the second water molecule could catalyze the decomposition of the HMHP product, possibly leading to formic acid or to formaldehyde and HOOH.

Finally, calculations predict that doubly substituted carbonyl oxides, such as acetone oxide, $(CH_3)_2COO$, should have small rate coefficients for reactions with water. As a result, their tropospheric removal may depend on other species and may be less efficient (20, 78). The calculations of Ryzhkov & Ariya (112) predict rate coefficients of $2.9 \times 10^{-19}$ cm³/s for reaction of $(CH_3)_2COO$ with the water monomer and $1.7 \times 10^{-16}$ cm³/s for reaction with the water dimer. The calculations of Anglada & Solé (109), which have given the largest rate coefficients, predict values of $4.0 \times 10^{-17}$ cm³/s with the monomer and $7.0 \times 10^{-13}$ cm³/s with the dimer. Huang et al. (31) noted that the reactions of Criegee intermediates with $SO_2$ were rapid for all Criegee intermediates, even those for which the reaction with water was unfavorable, and proposed that $(CH_3)_2COO$ could build to larger concentrations and be a potentially important oxidant of $SO_2$. They used direct ultraviolet absorption measurements of $(CH_3)_2COO$ and determined a rate coefficient of $1.3 \times 10^{-10}$ cm³/s for reaction with $SO_2$, significantly larger than for reactions of $CH_2OO$ or $CH_3CHOO$. They were unable to detect significant reaction with water up to relative humidity of 90%, implying an upper limit for the rate coefficient of $(CH_3)_2COO$ reacting with the water monomer of $1.5 \times 10^{-16}$ cm³/s and with the water dimer of $1.3 \times 10^{-13}$ cm³/s. With these rate coefficients, the reaction with water was predicted to be a relatively minor component of the tropospheric removal of $(CH_3)_2COO$ (31).

**Reactions with acids.** The reactions of Criegee intermediates with organic acids are extremely rapid, with rate coefficients in excess of $10^{-10}$ cm³/s (39, 120), far more rapid than reactions with carbonyls or the insertion reactions with water or the water dimer. Neeb et al. found that $CH_2OO$ was inserted into the O–H bonds of formic acid (121) and acetic acid (104) to form hydroperoxymethyl formate or hydroperoxymethyl acetate products. Long et al. (122) used CBS-QB3 methods to calculate stationary points for the eight possible entrance-channel complexes between $CH_2OO$ and formic acid, for cycloaddition across the C=O bond to form a hydroxylated secondary ozonide or insertion to produce a hydroperoxymethyl formate, and

of subsequent isomerization and dissociation channels. They found that the formation of the hydroperoxymethyl formate should be favored, a conclusion that matches the earlier results of Aplincourt & Ruiz-Lopez (123), who additionally calculated a substantial barrier to possible water elimination from hydroperoxymethyl formate to produce the formic acid anhydride observed in the experiments of Neeb et al. (121). However, the direct photoionization mass spectrometry measurements of Welz et al. (39) were unable to identify products of the reactions.

Kumar et al. (108) have calculated a different possible pathway in reactions of $syn$-$CH_3CHOO$, suggesting that the reaction with acids could proceed via an acid-catalyzed tautomerization of the Criegee intermediate to the VHP. The decomposition of the acid–Criegee adduct transfers the acidic hydrogen atom of the acid reactant to the terminal oxygen of the C−O−O of the Criegee intermediate, at the same time transferring a hydrogen from the C atom adjacent to the C−O−O group to the carbonyl oxygen of the acid. In a direct test of this hypothesis, Liu et al. (124) produced $CH_2OO$, $CH_3CHOO$, $(CH_3)_2COO$, and $CH_3CH_2CHOO$ by the diiodoalkane photolysis method and reacted them with deuterium-labeled formic and acetic acids, detecting the products by vacuum ultraviolet photoionization at 10.5 eV photon energy. The results show a striking difference between the reactions of $CH_2OO$, for which the tautomerization to a VHP is impossible, and of the other carbonyl oxides. For $CH_3CHOO$, $(CH_3)_2COO$, and $CH_3CH_2CHOO$, a clear product signal was observed, one mass unit higher than the initial Criegee intermediate mass, indicating an exchange of one hydrogen from the carbonyl oxide with one deuterium from the acid, just as would be expected in the acid-catalyzed tautomerization. In the case of $CH_2OO$ or of reaction with nondeuterated acids, no such peak appeared. This confirmation of the tautomerization pathway suggests that the products of the Criegee intermediate reactions with acids are not all formed via hydroperoxyester intermediates.

Inorganic acids are also a significant component in the troposphere, particularly in the urban boundary layer, and it would be expected that Criegee intermediates might also react rapidly with inorganic acids. Foreman et al. (125) measured the rate coefficients for $CH_2OO$ reacting with nitric acid and with hydrochloric acid. Both reactions are rapid, with the rate coefficient for reaction with HCl being $(4.6 \pm 1.0) \times 10^{-11}$ cm$^3$/s, and that for reaction with $HNO_3$ being ten times higher, $(5.4 \pm 1.0) \times 10^{-10}$ cm$^3$/s. Foreman et al. also carried out calculations of stationary points on the potential energy surfaces for both reactions. Neither reaction appears to have any significant barrier to formation of an initial complex or from the complex to the eventual products. The reactions with both acids are calculated to form hydroperoxide products—chloro(hydroperoxy)methane in the reaction with HCl and hydroperoxymethyl nitrate in the reaction with $HNO_3$—analogous to the reactions with other acids or with water. However, the nitric acid reaction is found to proceed by a different mechanism: Rather than insertion of $CH_2OO$ into the O–H bond of $HNO_3$, the reaction consists of a transfer of hydrogen from the $HNO_3$ to the terminal oxygen of the Criegee intermediate and of formation of a bond between the carbon atom and one of the other O atoms in the $HNO_3$.

## Addition to Radicals

Because Criegee intermediates are dominated by the closed-shell singlet zwitterion configuration, their reactions with radical species are not necessarily expected to be similar to typical radical–radical recombinations. The reaction of $CH_2OO$ with NO, for example, is calculated to have an entrance barrier (78) and has a rate coefficient less than $6 \times 10^{-14}$ cm$^3$/s (30, 68). The reactions of Criegee intermediates with $NO_2$ are more rapid, about $2 \times 10^{-12}$ cm$^3$/s (30, 35, 68), but still significantly lower than reactions with $SO_2$ or with acids. The assumed products of the Criegee

intermediate reactions with $NO_2$ are a carbonyl compound and nitrate radical ($NO_3$). Although some experiments seem to imply the formation of nitrate from reactions of Criegee intermediates with $NO_2$ (126, 127), other attempts to detect $NO_3$ in direct kinetic measurements have so far failed (30, 35). Stone et al. (68) reported a decrease in the production of the carbonyl coproduct, $CH_2O$, upon adding $NO_2$ to photolysis of $CH_2I_2$–$O_2$–$N_2$ mixtures, but suggested that this decrease could be attributable to reduced $CH_2O$ from side reactions. Moreover, Lewis et al. (117, p. 4862) recently stated that a forthcoming paper would show that $NO_3$ was "not significantly made by reaction of Criegee with $NO_2$." As in the case for many other reactions of Criegee intermediates, quantification of the products from carbonyl oxide reactions with $NO_2$, as a function of temperature and pressure, is needed to completely understand the reaction mechanism.

The inception and growth of atmospheric organic aerosols, a topic of enormous scientific interest and importance (128), is another area in which the reactions of Criegee intermediates could play a role (129, 130). Because ozonolysis is a prominent tropospheric oxidation process, atmospheric scientists need to understand how ozonolysis products may contribute to low-volatility products and condensation. Compositional analysis of aerosols that have been initiated by ozonolysis shows oligomers built from successive additions of the specific Criegee intermediate of the ozonolysis system (131–134).

A recent example from the Finlayson-Pitts group is shown in **Figure 6**. Oligomerization could occur from the insertion reactions of carbonyl oxides into hydroperoxides, which can form new hydroperoxides (as described above), or from the reactions of carbonyl oxides with alkylperoxy radicals, which form new alkylperoxy radicals. Vereecken et al. (78) calculated that the addition of alkylperoxy radicals to carbonyl oxides should be barrierless and predicted rate coefficients of $\sim 5 \times 10^{-12}$ cm$^3$/s for a generic reaction of a Criegee intermediate with an alkylperoxy radical. Anglada et al. (135) calculated a rate coefficient of $3.74 \times 10^{-12}$ cm$^3$/s for reaction of the formaldehyde oxide Criegee intermediate with the methylperoxy radical, and also predicted, on the basis of master equation calculations, that more than 85% of the product would be stabilized as the $CH_3OOCH_2OO$ adduct. Recall from above that Vereecken et al. (110) calculated similar rate coefficients for reactions of Criegee intermediates with alkyl hydroperoxides. No direct measurements of reactions of Criegee intermediates with alkylperoxy radicals (or hydroperoxides for that matter) have yet been reported, although this is clearly an opportunity for the methods of direct carbonyl oxide synthesis.

In experiments designed to distinguish between the alkylperoxy and alkyl hydroperoxide pathways, Zhao et al. (134) studied particle formation initiated by ozonolysis of *trans*-3-hexene in the presence of various scavengers for OH or Criegee intermediates. Because the OH scavengers (cyclohexane and chlorocyclohexane) produce different alkylperoxy radicals from each other and from the unperturbed ozonolysis, if Criegee intermediate reactions with alkylperoxy radicals were the initiating step for oligomerization, one would expect the oligomers in each system to be built upon different base species. As can be seen in **Figure 6**, this is in fact the case; when cyclohexane is added, the oligomer distribution shifts to include masses consistent with building from a cyclohexylperoxy radical, and when chlorocyclohexane is added, new peaks appear consistent with oligomerization starting at the chlorocyclohexylperoxy radical. However, the detected radicals are hydrogen terminated, so the oligomerization could also start with the hydrogen-terminated hydroperoxide (133). Zhao et al. provide evidence against this interpretation by also carrying out experiments with added formic acid, which would react with the Criegee intermediate to produce a new unique hydroperoxide product, and should seed its own oligomer chains if the hydroperoxide reaction were the major initiator. However, such oligomer chains were not discernible in the product spectrum, suggesting that the radical addition with Criegee intermediates is in fact the initiating step (134).
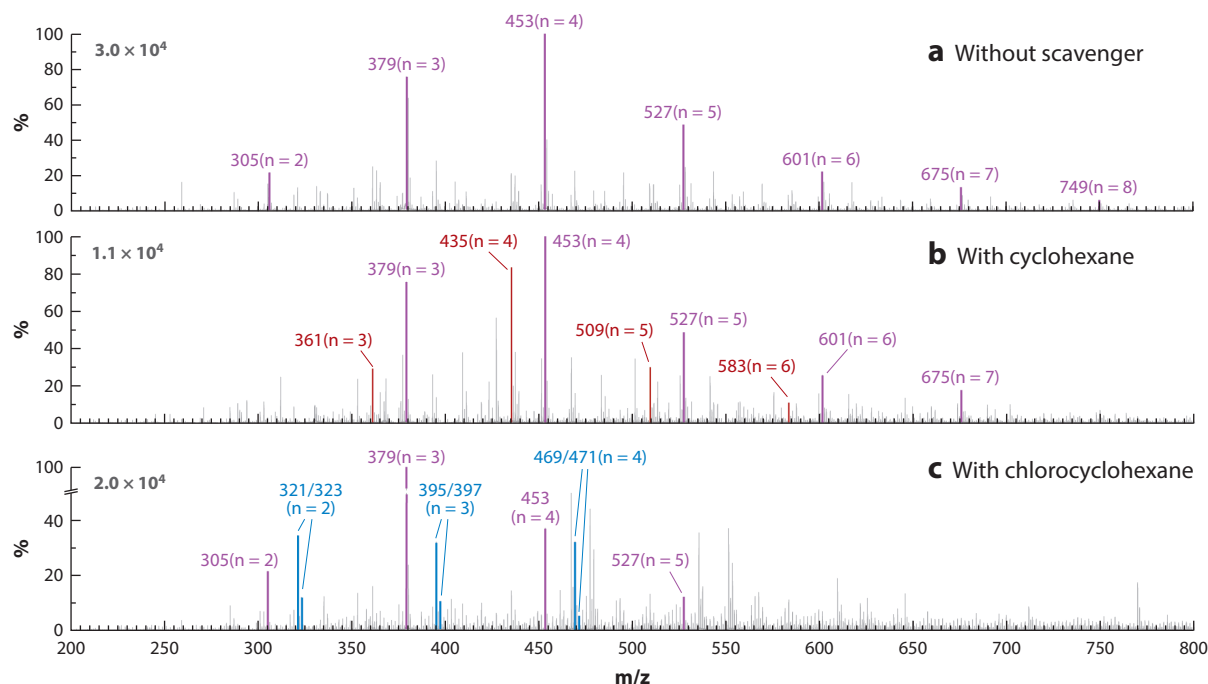
**Figure 6**

Mass spectrometric measurements of the composition of aerosols generated from ozonolysis of *trans*-3-hexene with and without the addition of OH scavengers (cyclohexane and chlorocyclohexane). The mass spectra exhibit oligomer sequences of the Criegee intermediate from 3-hexene ozonolysis. The OH scavengers produce distinct alkylperoxy radicals, and the particles generated show new oligomer sequences built on those characteristic alkylperoxy species. Figure adapted from Reference 134 with permission from the Royal Society of Chemistry.

Finally, in the context of atmospheric aerosols, the reactions of Criegee intermediates with surface- or particle-bound species have potential importance (136–140) and may provide a new opportunity for direct-synthesis methods. For example, Hearn et al. (138) studied the ozonolysis of oleic acid particles and methyl oleate particles. Measurements of ozone uptake by oleic acid on coated flow tubes showed a discrepancy with measurements of oleic acid removal by exposure to $O_3$, implying that more than one oleic acid molecule was consumed by each reacting ozone molecule. A comparison of oleic acid, which was expected to react with Criegee intermediates, and methyl oleate, which lacks acidic hydrogens and should react much more slowly with Criegee intermediates, showed that yields of a Criegee intermediate marker (a rearrangement product of the Criegee intermediate) was reduced by addition of oleic acid to methyl oleate particles, which established the reaction of Criegee intermediates at the interface. This comparison allowed a quantification of the secondary consumption of oleic acid by the carbonyl oxide ozonolysis products that reconciled the discrepancy in the ozone uptake measurements. However, the authors noted that they were not able to isolate a reaction rate coefficient for the Criegee intermediate at the interface from their data because they were not able to measure the pure Criegee intermediate concentration (138). The nature of carbonyl oxide interactions at interfaces or within particles is still more complex than the gas-phase ozonolysis process (139), but direct measurement of carbonyl oxide removal by surfaces could contribute to improving the analysis of particulate oxidation and aging.

## THE INCREASINGLY IMPORTANT ROLE OF THEORY

The investigations of Criegee intermediate chemistry have highlighted, as in many other areas of chemistry, the increasingly leading role of theory and computation. One prominent discovery of Criegee intermediate chemistry in the recent burst of research, the large rate coefficient for carbonyl oxide reactions with $SO_2$, was predicted by theory before experimental methods enabled a direct measurement, and detailed theory (77) is in excellent agreement with the experiments. Although rate coefficients, calculated by different methods, of the reactions of Criegee intermediates with water lay relatively far apart, they accurately predicted the relative reactivity of various carbonyl oxides. Again, recent calculations (116) are in good agreement with the measurements. This synergy between the measurements of isolated carbonyl oxide reactions and their theoretical descriptions is an important benefit of direct production and detection of Criegee intermediates. The direct experimental methods are able to isolate chemical processes that were previously entangled in ozonolysis and to compare them straightforwardly to the theoretical description of the same isolated process. The comparison has allowed an assessment of what levels of electronic structure theory and theoretical kinetics methods are necessary to accurately calculate reactions of these species. The validation of theory by direct experiment can therefore extend the impact of the direct measurements to systems that are not yet easily accessible by experimental methods.

## CONCLUSIONS

The ability to directly synthesize and interrogate gas-phase carbonyl oxides has rapidly led to a substantial improvement in our knowledge about many of their important unimolecular and bimolecular reactions. Moreover, experiments that isolate individual reactions of Criegee intermediates have confirmed the reliability of high-level quantum chemical calculations, coupled with accurate statistical kinetics methods, in predicting the behavior of carbonyl oxide reactions. However, such comparison with direct experiment, for example on the reactions with water, also highlights the challenges that theory faces in describing reactions of these inherently multi-reference species. Many areas of immediate interest are now open for investigation—the possible role for reactions of Criegee intermediates with radicals and hydroperoxides in the formation of organic aerosol, for example—and reactions of other Criegee intermediates, such as the carbonyl oxides from isoprene ozonolysis, will doubtless soon be directly studied.

These direct experiments build on and complement the ongoing careful study of ozonolysis processes. As discussed above, analyzing the consequences of Criegee intermediate reactions for tropospheric chemistry requires knowledge of the sources of carbonyl oxides as well as their removal reactions. The fraction of Criegee intermediates that are stabilized in alkene ozonolysis remains a subject of investigation (141), and the fate of chemically activated Criegee intermediates is not yet well understood. Direct detection of carbonyl oxides in gas-phase ozonolysis (50, 52) and the ability to directly synthesize, excite, and interrogate these intermediates (90, 96–99) may soon combine to resolve these questions.

## DISCLOSURE STATEMENT

## ACKNOWLEDGMENTS

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