

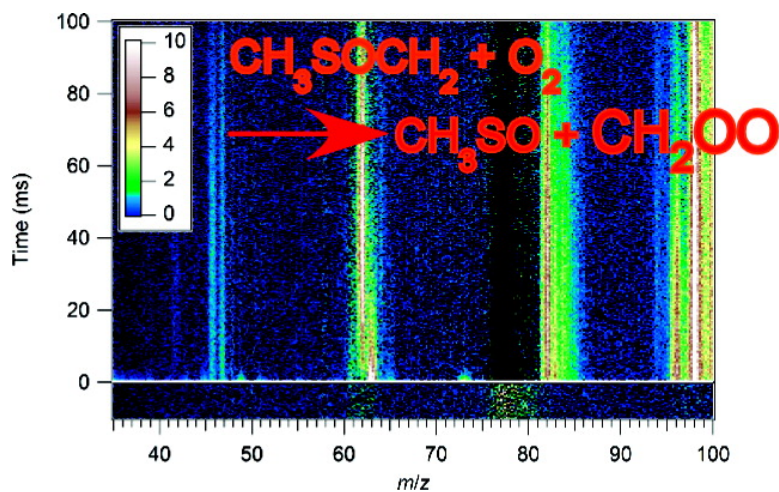
Communication

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Direct Observation of the Gas-Phase Criegee Intermediate (CH_2OO)

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The tropospheric oxidation of hydrocarbons is closely tied with the photochemistry of air pollution,¹ formation and aging of secondary organic aerosols,^{2,3} and haze formation.^{4,5} Reaction with ozone is an important removal mechanism for unsaturated hydrocarbons,⁶ which dominate biogenic hydrocarbon emissions⁷ and which are prominent intermediates in the oxidation of many other organic species. As first proposed by Rudolf Criegee,⁸ ozonolysis is generally accepted to occur via carbonyl oxide intermediates.⁹ Although gas-phase carbonyl oxides have never before been observed, and despite disagreement about their electronic structure,^{10–12} these “Criegee intermediates” are recognized as key species in, for example, tropospheric formation of organic acids^{9,13} and hydroperoxides.^{4,5}

The combination of tunable synchrotron photoionization with multiplexed mass spectrometry is capable of identifying even unexpected intermediates in complex systems.^{14,15} Experimental strategies for detection of the gas-phase Criegee intermediate must contend with the reactivity of the carbonyl oxide species and with the substantial internal excitation of the Criegee intermediate produced in most reactions. However, a recent study¹⁶ suggested that the reaction of $\text{CH}_2\text{S}(\text{O})\text{CH}_3$ with O_2 , an early step in the oxidation of dimethyl sulfoxide (DMSO), could produce formaldehyde oxide with little excess energy. We directly observed the Criegee intermediate by using photoionization to probe the chemical products of photolytically initiated DMSO oxidation, where production of Cl atoms by a pulsed laser starts the reaction, and the full mass spectrum of the reacting mixture is measured as a function of time and photoionization energy.¹⁷

A section of the time-resolved mass spectrum for the Cl-initiated oxidation of DMSO is shown in Figure 1. Prephotolysis signals have been subtracted. The chemistry is complex, but all of the observed product species can be identified based on their mass-to-charge ratio (m/z) and their photoionization efficiency spectra (see Figures S1–S8 in Supporting Information). Dimethyl sulfide (DMS) (CH_3SCH_3 , $m/z = 62$) is not seen in a neat DMSO flow but is observed in the reactor even without photolysis, possibly from reaction of the Cl precursor, oxalyl chloride, with DMSO. Products of Cl reactions with DMS, such as CH_3SCl and $\text{CH}_3\text{SCH}_2\text{Cl}$, are also identified. Formation of CH_3SO ($m/z = 63$), the coproduct of the Criegee intermediate in the $\text{CH}_3\text{SOCH}_2 + \text{O}_2$ reaction, occurs soon after photolysis and is strongly dependent on O_2 concentration (Figures S12–S13 of Supporting Information).

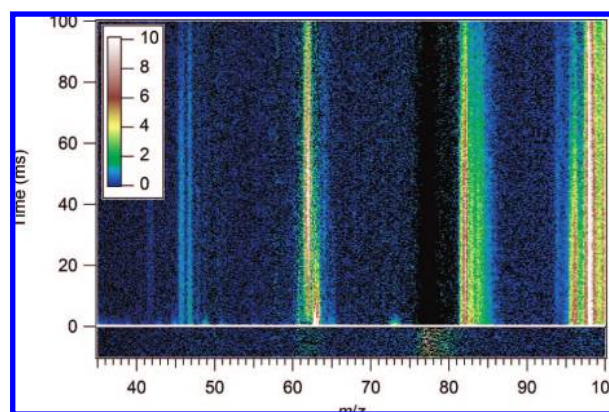


Figure 1. Section of the time-resolved mass spectrum, integrated over photoionization energy from 9 to 10.9 eV, of photolytic Cl-initiated oxidation of dimethyl sulfoxide (DMSO). The zero of time is set by the firing of the photolysis laser, which produces Cl atoms and initiates the reaction. The average prephotolysis signals have been subtracted from the spectrum, and negative resultants are shown as black.

The photoionization efficiency spectrum of the $m/z = 46$ product, integrated over reaction times between 0 and 60 ms, is shown in Figure 2. Thioformaldehyde (CH_2S) is readily recognized as a prominent component of this spectrum by comparison with its known photoionization efficiency curve.¹⁸ The two curves have been scaled to match each other in the plateau between 9.4 and 9.75 eV; CH_2S photoionization spectra taken in Cl-initiated DMSO oxidation under conditions where CH_2OO is negligible (see Figure S11 in Supporting Information) agree very closely with the higher resolution (~ 7 meV) Ruscic and Berkowitz¹⁸ spectrum. However, in Figure 2 an additional feature near 9.85 eV is evident in the DMSO oxidation. We attribute this feature to ionization of the Criegee intermediate, formaldehyde oxide. Unfortunately, the signal-to-noise ratio is insufficient to analyze the time behavior of this additional feature. Nevertheless, the feature seems to disappear at longer times, suggesting that the Criegee intermediate is formed soon after photolysis and is consumed during the subsequent chemistry. The $m/z = 46$ photoionization efficiency spectrum integrated over latest reaction times (e.g., from 55 to 100 ms after photolysis, the inset in Figure 2) is almost entirely due to CH_2S . The solution-phase reactions of sulfoxides with diphenylcarbonyl oxide yield the corresponding sulfides and sulfones,¹⁹ so it is possible that some of the dimethyl sulfide or dimethyl sulfone ($m/z = 94$) observed in the present experiments (Figure 1 and Supporting Information) is from reaction of CH_2OO with DMSO.

The difference between the $m/z = 46$ photoionization efficiency spectrum from DMSO oxidation and the reference CH_2S spectrum¹⁸

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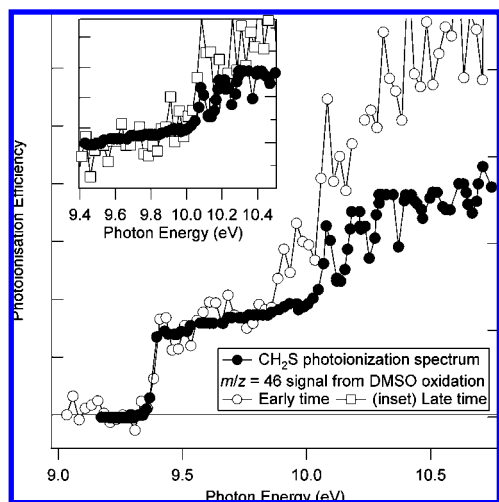


Figure 2. Photoionization efficiency (PIE) spectrum of the $m/z = 46$ signal observed in the Cl-initiated oxidation of DMSO, integrated over the first 50 ms following the photolysis pulse (○). (●) PIE spectrum of CH_2S from Ruscic and Berkowitz.¹⁸ The difference between the two spectra is attributed to ionization of the Criegee intermediate CH_2OO . As shown in the inset, the feature near 9.85 eV is markedly less apparent in the spectrum obtained by integration over reaction times from 55 to 100 ms after photolysis (□).

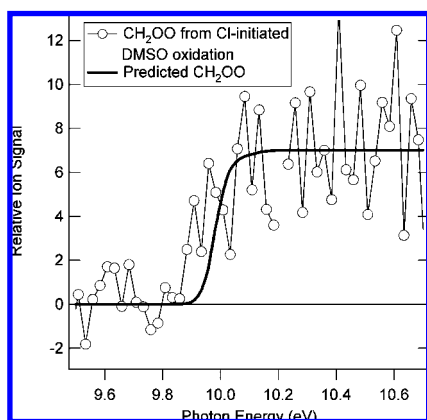


Figure 3. Photoionization efficiency spectrum of the Criegee intermediate CH_2OO (formaldehyde oxide), observed in the Cl-initiated oxidation of DMSO (○). The predicted photoionization efficiency spectrum, based on high-level ab initio calculations¹¹ and density functional theory (B3LYP) geometry, frequency, and force constant evaluations, is shown as the solid line.

is shown in Figure 3. The identification of the carrier of this residual photoionization feature as CH_2OO is based in part on the qualitative chemical kinetics, but more decisively on the close agreement between observed and computed photoionization efficiency spectra and on the elimination of other possibilities. The contribution of thioformaldehyde¹⁸ has been subtracted. The other conceivable molecular sources of signal at $m/z = 46$ (and composed of carbon, oxygen, sulfur, and hydrogen) are formic acid, ethanol, dimethyl ether, and dioxirane. These molecules have experimentally known^{20,21} or calculated¹¹ ionization energies that are higher than that of the $m/z = 46$ species observed in the DMSO oxidation and can therefore be ruled out.

To identify the feature at $m/z = 46$, the overall shape and onset of the unknown photoionization efficiency spectra of the two $m/z = 46$ species formaldehyde oxide and dioxirane have been computed. Optimized molecular parameters from the CBS-QB3 composite method²² are employed in a spectral simulation that is

carried out by computation and integration of the photoelectron spectra²³ of the species within the Franck–Condon approximation. There is little difference in geometry between the neutral CH_2OO ($^1\text{A}'$) and cation CH_2OO^+ ($^2\text{A}'$), resulting in an intense 0–0 vibronic transition and a sharp ionization threshold. For dioxirane there is an increase in the C–O bond distance of 0.06 Å upon photoionization, yielding an extended vibrational progression and a more gradual onset of ionization than for CH_2OO (Figure S14 of Supporting Information). The CBS-QB3 adiabatic ionization energies (AIE) of 10.02 eV for CH_2OO and 10.84 eV for dioxirane are expected to be accurate to within 10 kJ mol⁻¹ (0.1 eV), and they agree well with higher-level CCSD(T)/CBS calculations¹¹ that yield AIE of 9.98 eV for CH_2OO and 10.82 eV for dioxirane. The simulation for CH_2OO ionization at 300 K, using CBS-QB3 optimized geometries, frequencies, and force constants with CCSD(T)/CBS energies,¹¹ and convolved with the measured experimental resolution of 50 meV, is shown as the solid line in Figure 3. The computed spectrum agrees closely in both shape and energy position with the feature assigned as the Criegee intermediate. The experimental ionization energy appears to be ~0.02 eV lower than the CCSD(T)/CBS value, well within the expected uncertainty in the calculation.

Dissociative ionization of other species to form CH_2S^+ is a possible source of the observed $m/z = 46$ feature. However, several considerations argue against such an explanation in the present case. First, the sharp onset in the photoionization efficiency is characteristic of a direct molecular ionization, and is unlikely in any dissociative ionization process. Second, the photoionization efficiency spectrum at $m/z = 48$ ($\text{CH}_2^{34}\text{S}^+$) shows no sign of the feature attributed to CH_2OO (see Figure S9 in the Supporting Information), albeit at too low a signal-to-noise ratio to be definitive. Furthermore, the observed CH_2OO ionization threshold is much lower than the appearance energies of CH_2S^+ from the other observed species,^{18,20} with the exception of $\text{CH}_3\text{SCH}_2\text{Cl}$, which could dissociatively ionize to CH_2S^+ and HCl with an energetic threshold (CBS-QB3) near 9.9 eV (the CBS-QB3 calculated thresholds for CH_2S^+ formation are 10.20 eV from $\text{CH}_3\text{SCH}_2\text{Cl}$, 10.67 eV from CH_3SH , and 11.66 eV from CH_3SO). However, in the present measurements under various conditions, the amplitude of the CH_2OO^+ feature was completely uncorrelated with that of the $\text{CH}_3\text{SCH}_2\text{Cl}^+$ signal (Figures S10–S11 of Supporting Information). Ruscic and Berkowitz¹⁸ used pyrolysis of $\text{CH}_3\text{SCH}_2\text{Cl}$ as a source of CH_2S for their photoionization efficiency measurements and did not report any contribution from dissociative ionization of the precursor, and, furthermore, direct photoionization of $\text{CH}_3\text{SCH}_2\text{Cl}$ shows no $m/z = 46$ signal at 10 eV.²⁴ Finally, the loss of the CH_2OO feature at long reaction time precludes its arising from dissociative ionization of a persistent product. The only feasible explanation for the $m/z = 46$ feature appears to be photoionization of the Criegee intermediate.

Whether the isolated Criegee intermediate exists as a zwitterion or a biradical has been controversial,^{10,12} with recent calculations¹¹ establishing a polar structure with considerable zwitterionic character. In fact, calculations by Gutbrod et al.²⁵ show that alkyl substitution further favors the zwitterionic configuration. The photoionization efficiency spectrum is sensitive to the changes in geometry and vibrational frequencies upon ionization, which differ between the two structures. The observation of nearly vertical ionization for CH_2OO , as predicted by the polar structure, gives experimental corroboration of substantial charge separation in gas phase CH_2OO .

Another immediate implication of the detection of formaldehyde oxide is the possibility of determining Criegee intermediate

production in controversial systems, such as the proposed formation of CH₂OO in low-temperature combustion of dimethyl ether.²⁶ In that technologically important system, the Criegee intermediate could be a marker for the critical chain branching steps that proceed via O₂ addition to an ephemeral •CH₂OCH₂OOH intermediate.²⁶ Furthermore, detection of CH₂OO will enable direct measurement of kinetics of atmospherically important reactions of Criegee intermediates with species such as SO₂, water, aldehydes, and nitrogen oxides. These reactions affect tropospheric levels of HO_x,²⁷ organic acids,¹³ peroxides,^{4,5} and secondary organic aerosols,^{2,3} but their rate coefficients are poorly characterized,¹³ and product branching fractions are largely unknown. Direct measurement of bimolecular reactions and particularly unimolecular decomposition of Criegee intermediates could reduce uncertainty in atmospheric models.

The current CH₂OO measurements have signal-to-noise too low to be useful for kinetics. Prospects for improved Criegee-intermediate detection to be pursued with future synchrotron time include optimization of the DMSO oxidation chemistry for CH₂OO, perhaps by employing other photolyses. The major interference in the present experiments is the formation of thioformaldehyde. Thioformaldehyde might be a product of CH₃SOCH₂ reactions. Alternatively, if CH₂S is largely formed by reactions of dimethyl sulfide, other systems that exhibit less dark formation of DMS may be advantageous. Finally, the observation of Criegee intermediate in the present reaction system may open the way for detection of CH₂OO by other spectroscopic means.¹⁰

The present experiments used DMSO oxidation as a convenient means to produce stabilized CH₂OO. Dimethyl sulfoxide is a key intermediate in the oxidation of dimethyl sulfide, which constitutes a substantial portion of the global sulfur budget.²⁸ Criegee intermediate production in DMSO oxidation could affect models for aerosol chemistry, organic acid production, and formation of peroxides, particularly in the marine boundary layer. The principal role for Criegee intermediates in current atmospheric chemistry models is not associated with sulfur chemistry but rather with ozonolysis.^{1,6} The formation of CH₂OO + CH₃SO from CH₃S(O)CH₂ + O₂ is about 12.5 kcal mol⁻¹ exothermic.¹⁶ Criegee intermediates from ozonolysis are substantially more energetic, but substantial yields of stabilized intermediates are possible.²⁹ Direct detection of OH formation from excited substituted Criegee intermediates would be particularly valuable; however, the intermediates that form OH are correspondingly more difficult to stabilize from ozonolysis.

Although the formation of carbonyl oxide species in ozone + alkene reactions no longer excites significant controversy,⁹ these intermediates have never been directly observed in gas phase ozonolysis. Ozonolysis is not readily investigated in the present apparatus, and the current measurements do not provide direct verification of the Criegee mechanism. Nevertheless, this work allows a reinterpretation of previous investigations that gives possible confirmation of formaldehyde oxide formation in ethene ozonolysis. Martinez et al.³⁰ measured a mass 46 species in Ar-lamp (11.7 and 11.8 eV lines) photoionization mass spectrometry analysis of cryogenically trapped products from low-temperature ozonolysis of ethene. They assigned the species as dioxirane, based on the microwave spectroscopic identification by Lovas and Suenram³¹ in a similar system. However, Martinez et al.³⁰ also observed a small *m/z* = 46 product signal when using a Kr lamp (photon energies of 10.6 and 10.0 eV). They therefore suggested that the ionization energy of dioxirane was 10.6 eV or lower. Based

on the present observation of the carbonyl oxide photoionization, with an ionization energy of approximately 10 eV and the computed ionization energy of dioxirane of 10.82 eV,¹¹ it appears likely that the earlier measurements intercepted stabilized CH₂OO from the ozonolysis.

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Supporting Information Available: Detailed experimental method; Figures S1–S14; full refs 7 and 22. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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