Direct Kinetic Measurements of Criegee Intermediate (CH$_2$OO) Formed by Reaction of CH$_2$I with O$_2$

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posited by the cellulose microfibrils specially arranged on the plant cell wall lead to complex actuation behavior. Likewise, we demonstrate that PVA hydrogel films containing reinforcing platelets with gradually changing local orientation can reversibly change their shape from straight to well-defined wavy patterns upon drying or swelling of the hydrogel matrix (Fig. 4F).

Given the possibility to precisely control the position and orientation of reinforcing particles within the matrix, the method outlined here offers a way to locally tailor the properties of composite materials by using the same set of initial building blocks. The myriad of unusual properties including out-of-plane global or local increases in composite stiffness, strength, hardness, wear resistance, and the shape memory effect achieved by simply controlling the orientation and position of reinforcing elements suggest the enormous potential of this approach.

References and Notes

27. Materials and methods are available as supporting material on Science Online.

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Direct Kinetic Measurements of Criegee Intermediate (CH2OO) Formed by Reaction of CH2I with O2

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Ozonolysis is a major tropospheric removal mechanism for unsaturated hydrocarbons and proceeds via “Criegee intermediates”—carbonyl oxides—that play a key role in tropospheric oxidation models. However, until recently no gas-phase Criegee intermediate had been observed, and indirect determinations of their reaction kinetics gave derived rate coefficients spanning orders of magnitude. Here, we report direct photoionization mass spectrometric detection of formaldehyde oxide (CH2OO) as a product of the reaction of CH2I with O2. This reaction enabled direct laboratory determinations of CH2OO kinetics. Upper limits were extracted for reaction rate coefficients with NO and H2O. The CH2OO reactions with SO2 and NO2 proved unexpectedly rapid and imply a substantially greater role of carbonyl oxides in models of tropospheric sulfate and nitrate chemistry than previously assumed.

In 1949, Rudolf Criegee proposed that ozonolysis of alkenes proceeds via carbonyl oxide biradicals, in an ozonolysis mechanism that is now generally accepted (1). Because a large fraction of the tropospheric oxidation of unsaturated hydrocarbons is initiated by reaction with ozone (2), these biradical “Criegee intermediates” play a substantial role in the tropospheric budgets of secondary organic aerosols (SOAs), ozone, NOx, NOx, and HOx. For example, the OH radical, key to the oxidizing capacity of the troposphere, is formed by a sequence of photochemical reactions involving ozone:

$$O_3 + h\nu \rightarrow O(1D) + O_2 \quad (1)$$
$$O(1D) + H_2O \rightarrow OH + OH \quad (2)$$

These reactions depend on the presence of sunlight and water vapor. However, field measurements (3) have shown that OH levels in winter and summer are very similar in UK urban environments (4), despite the fact that in winter the efficiency of the reaction in Eq. 1 drops by at least 50%. Harrison et al. (4) showed that winter production of OH via ozonolysis of alkenes, dominated by Criegee radical chemistry, makes up this difference. SOAs can also be initiated by Criegee intermediate reactions (5, 6).

Although decades of theoretical studies and indirect experimental evidence support the importance of Criegee radicals in the troposphere [e.g., (7)], the quantitative effects of their chemistry remain uncertain (8) because it has been impossible to make direct measurements of Criegee reactions with key atmospheric species. Until now, determination of rate constants for Criegee reactions has been carried out by investigating changes in the products of ozonolysis upon addition of different reagents or scavengers (9, 10). Interpretation of such experiments requires modeling the full complexity of ozonolysis, in which the production, stabilization, and removal of Criegee intermediates are all imperfectly understood. Although an internally consistent picture of Criegee chemistry has been slowly emerging (11), absolute rate coefficient estimates with key atmospheric species continue to range over 4 to 5 orders of magnitude (12).

Recently the photoionization spectrum of the simplest gas-phase Criegee intermediate, formaldehyde oxide (which we denote as CH2OO), was measured in the chlorine atom-initiated oxidation of dimethyl sulfoxide (DMSO) (13). In

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**References and Notes**

the present work, another pathway to stabilized CH2OO is demonstrated: the reaction of CH2I with O2. The iodomethyl radical, CH2I, is an important intermediate in the breakdown of organic iodides, and its dominant fate is reaction with O2 (14). The CH2I and O2 reaction has several possible product channels:

\[
\begin{align*}
\text{CH}_2\text{I} + \text{O}_2 & \rightarrow \text{CH}_2\text{OO} \quad (3a) \\
\text{CH}_2\text{I} + \text{O}_2 & \rightarrow \text{CH}_2\text{O} + \text{IO} \quad (3b) \\
\text{CH}_2\text{I} + \text{O}_2 & \rightarrow \text{I} + \text{CH}_2\text{O}_2 \text{ (various isomers)} \quad (3c)
\end{align*}
\]

Eskola et al. (15) used laser photolytic initiation and photoionization mass spectrometric detection to study this reaction and found that atomic iodine (channel 3c) is the principal direct product of the reaction at low pressures. We find that the coproduct isomer is CH2OO and that it can be formed in sufficient quantities to carry out direct chemical kinetics studies.

In the present experiments, CH2I was produced by 248-nm photolysis of diiodomethane, CH2I2, at 298 K and 4 torr, in a large excess of O2. The reacting mixture was interrogated by tunable synchrotron photoionization mass spectrometry. A time-resolved mass spectrum from the CH2I2/O2 system is shown in Fig. 1. The resolution of the mass spectrometer is sufficient to establish that the nominal mass/charge (m/z) = 46 peak arises from CH2O2 and not, for example, C2H5O (fig. S1). The formation rate of the m/z = 46 species is correlated with the disappearance rate of CH2I (m/z = 141) (figs. S2 to S4), establishing that CH2OO is a direct product from the reaction of CH2I with O2. Tuning the synchrotron photon energy allows a photoionization spectrum of the m/z = 46 species to be measured (Fig. 2). The photoionization spectrum agrees with that measured for CH2OO in chlorine-initiated DMSO oxidation (13) and with CCSD(T)/CBS (coupled-cluster with single and double excitations and perturbative treatment of triple excitations/complete basis set extrapolation) calculations for the CH2OO ionization energy (expected to be accurate to 0.05 eV) (16). Dioxirane and formic acid have much higher ionization energies, 10.82 eV and 11.33 eV (16, 17). The mass and the photoionization spectrum support unambiguous assignment of the product as formaldehyde oxide, CH2OO. A small formic acid signal is observed at longer times (fig. S5), which could be produced by reaction of the Criegee intermediate.

The longest CH2OO lifetime observed, \( \tau \approx 2 \text{ ms} \) (Fig. 3), is well below estimates for thermal isomerization or dissociation of CH2OO (18, 19). Changes in decay rates with different wall coatings [supporting online material (SOM) text] suggest that heterogeneous loss contributes to CH2OO removal in these experiments. Formaldehyde (CH2O) formation is correlated with the disappearance of CH2OO, implying that most of the formaldehyde is produced by reactions of the Criegee intermediate rather than from the direct reaction of CH2I with O2. This observation is consistent with the conclusions of other researchers (20, 21) that channel 3b is minor. The experimental lifetime is long enough to allow direct pseudo-first-order measurements of relatively rapid reactions of CH2OO. We have carried out such measurements of Criegee intermediate reactions with SO2, NO2, NO, and H2O.

Addition of SO2 and NO2 produced a more rapid decay of CH2OO, as shown in Fig. 3 for the SO2 reaction and in fig. S9 for the NO2 reaction. For measurements of the reaction with NO and NO2, 13CH2OO was used because 14NO2 appears at nearly the same mass as 13CH2OO. The 13C kinetic isotope effect is expected to be far smaller than the experimental uncertainties in the rate coefficient measurements. The reciprocal of the lifetime of CH2OO is linearly related to the excess reactant concentration, with the second-order rate coefficient as the slope (Fig. 4 and fig. S10).

The final analysis (SOM text) yields rate coefficients at 298 K (and 4 torr) of 3.9 \( \times 10^{-11} \text{ cm}^3 \text{ s}^{-1} \) (95% uncertainty) for CH2OO with SO2 and 7 \( \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) for 13CH2OO with NO2, with asymmetric 95% uncertainty bounds of \( +3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \) and \( -2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \). These rate coefficients are from 50 to 10,000 times larger than estimates typically used in tropospheric models (7, 8). The reaction of CH2OO with NO2 (22) has additional laboratory relevance because it has been used to scavenge Criegee intermediates and as a reference for measurements of other Criegee reactions. Recent theoretical work (23) has estimated a nearly collision-limited rate coefficient (\( \sim 4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \)) for the reaction of CH2OO with NO2, much higher than previous experiments but within a factor of 10 of the present direct measurements. The ratio of initial CH2OO to final CH2O amplitudes changes little upon addition of SO2 (fig. S14), suggesting that SO2 plus CH2O is a product channel.

Addition of NO up to [NO] = 5 \( \times 10^{15} \text{ cm}^{-3} \) or H2O up to [H2O] = 3 \( \times 10^{16} \text{ cm}^{-3} \) produced no measurable increase in the decay rate of CH2OO (figs. S11 to S13). Reaction of NO with CH2OO is postulated to form CH2O and NO2 (8); however, no product formation could be observed in these experiments. The reaction of CH2OO with water is thought to produce hydroxy-methylhydroperoxide (HOCH2OOH, HMHP) by association (24) or to catalyze isomerization (25). The photon energy of the measurements, 10.5 eV, is well below the ionization energy of formic acid (17) and dioxirane (16) (Fig. 2), so the isomerization channel would still lead to a loss of photoionization signal at m/z = 46. The photoionization behavior of HMHP is unknown, but at the highest water concentrations a very faint product signal, much too small for kinetic analysis, can be observed at m/z = 64.

Assuming that a change of 25% in the decay rate constant of CH2OO would be readily detectable, the maximum concentrations of H2O and NO used in conjunction with the observed
zero-reagent decay constants (~500 s⁻¹ for the water experiments, ~1100 s⁻¹ for the NO experiments) give upper limits of $k(H_2O) < 4 \times 10^{-15}$ cm³ s⁻¹ and $k(NO) < 6 \times 10^{-14}$ cm³ s⁻¹. The upper limit for reaction with water is above literature estimates of the rate constant (12) and tends to confirm the established models. On the other hand, the reaction with NO is two orders of magnitude slower than literature estimates (2).

The direct determinations of the rate constants for CH₂OO with SO₂ and NO₂, however, are considerably higher than previous estimates. Placing the present results into a tropospheric chemistry model (26) implies a substantial role of Criegee intermediates in sulfate and nitrate chemistry. Steady-state analysis (SOM text) shows that, if the rate coefficient for other Criegee intermediates is similar to that for CH₂OO, Criegee intermediates could be at least as important an oxidizer of SO₂ as OH across much of the terrestrial boundary layer. Reaction of Criegee intermediates with NO₂ may be an important daytime and nighttime source of nitrate radical. The present rate coefficient for the Criegee plus NO₂ reaction would increase the modeled NO₃ concentration by up to 20%, the enhancement scaling linearly with alkene concentration.

**Fig. 2.** Photoionization spectrum of the mass = 46 product of the CH₂I plus O₂ reaction, integrated over the first 2 ms after photolysis. The calculated photoionization spectra of the Criegee intermediate CH₂OO and dioxirane (13), the experimental photoionization spectrum for formic acid (17), as well as schematic chemical structures, are shown for reference.

**Fig. 3.** Time-dependent CH₂OO signal for various concentrations of SO₂. Solid lines represent fits to the data traces, including convolution with a measured instrument response function (SOM text), from which pseudo–first-order decay constants are derived.

Low-volatility products, such as organic acids or hydroperoxides, of unimolecular and bimolecular Criegee reactions contribute to organic aerosol formation (7, 27). The production of a Criegee biradical from the CH₂I plus O₂ reaction might affect modeling of oxidation and aerosol chemistry in the marine boundary layer (28). The exothermic (16) formation of CH₂OO plus I will compete with stabilization to CH₂IO₂, so full assessment of that impact will require measurements of branching fractions at atmospheric pressure. The demonstration that CH₂I and O₂ forms a Criegee intermediate as the dominant, if not sole, CH₂O₂ isomer indicates broad utility for Criegee chemistry investigations. For example, it may be possible to determine optical spectra for gas-phase CH₂OO by using this reaction; reported measurements of product ultraviolet spectra from CH₂I and O₂ (20, 29) may already include contributions from the Criegee intermediate. Direct optical monitoring of Criegee intermediates could probe Criegee formation and reaction at atmospheric pressure. Additionally, reactions of other α-iodoalkyl radicals with O₂ may be used to form substituted Criegee intermediates and investigate their kinetics.

Reaction rate coefficients under tropospheric conditions are pressure- and temperature-dependent, and reactions are commonly affected by the presence of water and the participation of weakly bound complexes (30, 31). Measurement of rate coefficients at one set of conditions, as in this work, does not completely characterize a reaction; for example, if the reactions have a substantial stabilization component, the rate constants could be substantially larger at atmospheric pressure. Decades of ozonolysis studies have mapped a web of dependencies on conditions and scavenger species (31). The combination of a method for stabilized Criegee production and unambiguous photoionization detection of Criegee intermediates now enables direct study of these complicated relationships.

**Fig. 4.** Dependence of the pseudo–first-order Criegee intermediate decay constant (reciprocal of the lifetime $\tau$) on the concentration of SO₂. Error bounds are 95% uncertainty estimates based on least-squares analysis of the unweighted fits as depicted in Fig. 3, which include >20 points across the relevant decay. The second-order rate coefficient is given by the slope of the linear fit.
Sucrose Efflux Mediated by SWEET Proteins as a Key Step for Phloem Transport

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Plants transport fixed carbon predominantly as sucrose, which is produced in mesophyll cells and imported into phloem cells for translocation throughout the plant. It is not known how sucrose migrates from sites of synthesis in the mesophyll to the phloem, or which cells mediate efflux into the apoplasm as a prerequisite for phloem loading by the SUT sucrose–H⁺ (proton) cotransporters. Using optical sucrose sensors, we identified a subfamily of SWEET sucrose efflux transporters. AtSWEET11 and 12 localize to the plasma membrane of the phloem. Mutant plants carrying insertions in AtSWEET11 and 12 are defective in phloem loading, thus revealing a two-step mechanism of SWEET-mediated export from parenchyma cells feeding H⁺-coupled import into the sieve element–companion cell complex. We discuss how restriction of intercellular transport to the interface of adjacent phloem cells may be an effective mechanism to limit the availability of photosynthetic carbon in the leaf apoplast in order to prevent pathogen infections.

Breeding has led to marked increases in crop yield. Increased yield potential has mainly been attributed to improvements in allocation efficiency, defined as the amount of total biomass allocated into harvestable organs (1, 2). Despite the critical importance of sucrose translocation in this process, we do not understand mechanistically how changes in translocation efficiency may have contributed to an increase in harvestable products. Allocation of photosynthates in plants is conducted by transport of sucrose from the photosynthetic “sources” (predominantly leaves) to the heterotrophic “sinks” (meristems, roots, flowers, and seeds) (3–5). Sucrose, the predominant transport form of sugars in many plant species [see (6) for an overview of the different sugars and translocation mechanisms], is produced in leaf mesophyll cells, particularly in the palisade parenchyma of dicots and the bundle sheath of monocots.

In apoplastic loaders, sucrose is loaded into the sieve element–companion cell complex (SE/CC) in the phloem by the sucrose-H⁺ co-transporter SUT1 (named SUC2 in Arabidopsis) from the apoplasm (cell wall space) (7–11). However, sucrose must effuse from inside the cell into the cell wall, either directly from mesophyll cells (after which it travels to the phloem in the apoplasm) or from cells closer to the site of loading (having traveled cell-to-cell through plasmodesmata). Both the site and the mechanism of sucrose efflux remain to be elucidated, although it has been argued that a site in the vicinity of the site of phloem loading is most probable (4, 5).

We identified proteins that can transport sucrose across the plasma membrane: AtSWEET10 to 15 in Arabidopsis and OsSWEET11 and 14 in rice (Oryza sativa). We found that AtSWEET11 and 12 are expressed in phloem cells, and that inhibition by mutation reduces leaf assimilate exudation and leads to increased sugar accumulation in leaves. Thus, apoplastic phloem loading occurs in a two-step model: Sucrose exported by SWEETs from phloem parenchyma cells feeds the secondary active proton-coupled sucrose transporter SUT1 in the SE/CC.

The sucrose efflux transporters were identified by means of a Förster resonance energy transfer (FRET) sensor-based screen. Because humans do not seem to possess sucrose transporters, we reasoned that human cell lines should lack endogenous sucrose transport activity and should thus represent a suitable functional expression system for heterologous sucrose transporters. A preliminary set of ~50 candidate genes encoding membrane proteins with unknown function as well as members of the recently identified SWEET glucose efflux family (12) were coexpressed with the FRET sucrose sensor FLIPsuc90∆A1V (13) in human embryonic kidney (HEK) 293T cells. AtSWEET10 to 15, which all belong to clade III of the AtSWEET family

References and Notes

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