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**Infrared Absorption Spectrum of the Simplest Criegee Intermediate CH$_2$OO**

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The Criegee intermediates are carbonyl oxides postulated to play key roles in the reactions of ozone with unsaturated hydrocarbons; these reactions constitute an important mechanism for the removal of unsaturated hydrocarbons and for the production of OH in the atmosphere. Here, we report the transient infrared (IR) absorption spectrum of the simplest Criegee intermediate CH$_2$OO, produced from CH$_2$I + O$_2$ in a flow reactor, using a step-scan Fourier-transform spectrometer. The five observed bands provide definitive identification of this intermediate. The observed vibrational frequencies are more consistent with a zwitzen than a biradical structure of CH$_2$OO. The direct IR detection of CH$_2$OO should prove useful for kinetic and mechanistic investigations of the Criegee mechanism.

The gaseous reactions of ozone (O$_3$) with unsaturated hydrocarbons have been extensively investigated, given their roles in atmospheric depletion of these molecules and associated build-up of OH free-radical and particulate material in the troposphere (1–3). In summer, the dominant OH-production channel in the atmosphere includes photolysis of ozone to produce O($^1$D), which subsequently reacts with H$_2$O to produce OH. During the winter season, the efficiency of ozone photolysis drops by 50% or more, and the atmospheric production of OH via ozonolysis of alkenes was proposed to account for the difference in the photolytic production of OH between summer and winter (4).

Decades of research suggest the initiation of the ozonolysis reactions involves the cycloaddition of ozone to the C=C double bond to form a cyclic trioxolane intermediate (ozonide) with a C=C single bond. The large exothermicity of this reaction leads to a rapid cleavage of this C=C bond and one O–O bond of the ozonide to form a carbonyl molecule and a carbonyl oxide that is commonly referred to as the Criegee intermediate, which was first postulated by Criegee in 1949 (5). The simplest ozone-alkene reaction involves ethene (C$_2$H$_4$); the products from fragmentation of ethene oxide (C$_2$H$_4$O$_2$) are formaldehyde (H$_2$CO) and formaldehyde oxide (or peroxymethylene, CH$_2$OO), which is hence the simplest Criegee intermediate.

The structure and reactions of gaseous Criegee intermediates have been extensively investigated and debated (6–9). Four isomers of CH$_2$OO include formaldehyde oxide, dioxirane, methylenebis(oxy), and formic acid (HCOOH), as shown in Fig. 1. The large exothermicity of the reaction of O$_3$ + C$_2$H$_4$ might lead to isomerization among these isomers and the decomposition of these species to produce H, OH, CH$_3$, CO, CO$_2$, and other products (1–3).

The highly reactive Criegee intermediates have until recently eluded detection in the gaseous phase. Taieb and co-workers produced CH$_2$OO from the reactions of CH$_2$SOCH$_3$ + O$_2$ (10) and CH$_3$I + O$_2$ (11) in a flow cell and detected its cation with vacuum ultraviolet photoionization. They confirmed that the Criegee intermediate, rather than other isomers, was observed because the observed photoionization threshold near 10 eV conforms to theoretical predictions of 9.98 eV (12), which is much smaller than the values of 10.82 eV predicted for dioxirane (13) and 11.3 eV determined for formic acid (13). Beames et al. used the CH$_3$I + O$_2$ reaction to prepare CH$_2$OO in a supersonic jet and reported that a broad ultraviolet (UV) spectrum of CH$_2$OO peaked near 335 nm; the spectrum was obtained through UV-induced depletion of the ion signal of CH$_2$OO produced upon photoionization (14). The infrared (IR) absorption spectrum of gaseous CH$_2$OO would supply more detailed structural information as well as an alternative means for performing kinetic measurements.

Theoretical investigations of the structure and reactivity of CH$_2$OO have been extensive (12, 15–18), but predictions of the enthalpy of formation, electronic structure, and vibrational wave numbers vary considerably. The reported enthalpy of formation of CH$_2$OO at 298 K, ΔH$_T^0$, varies from 26 to 48 kcal mol$^{-1}$ but settles toward the smaller value when more sophisticated methods are used. Earlier theoretical calculations indicated CH$_2$OO to have a planar, singlet biradical structure, with nearly equally long O–O and C–O bonds of about 1.34 Å (19), whereas coupled-cluster theory CCSD(T) and multiconfigurational complete active space self-consistent field (CASSCF) calculations predicted that CH$_2$OO is better described as a zwitzen with a shorter C–O bond (~1.28 Å) and a longer O–O bond (~1.35 Å) (Fig. 1A) (12, 16, 17). The vibrational frequencies predicted for CH$_2$OO also vary considerably. For example, predictions of the wave number of the O–O stretching mode ranged from 849 to 1077 cm$^{-1}$, and of the C–O stretching mode from 1269 to 1407 cm$^{-1}$.

Because CH$_2$OO is unstable, its detection with a conventional Fourier-transform IR (FTIR) spectrometer is difficult. We have demonstrated that coupling a step-scan FTIR spectrometer with a multipass absorption cell enables the recording of temporally resolved IR absorption spectra of gaseous reaction intermediates such as CICO (20) and CH$_2$OO (21); distinct absorption bands of various isomers of CH$_2$SO (22), CH$_3$OO (23), and CH$_3$OSO (24) were recorded to provide definitive structural identification. Here, we report a further application of this technique to characterize the IR absorption spectra of gaseous CH$_2$OO species.

A step-scan FTIR [Vertex 80v (Bruker Optik, Ettlingen, Germany)] spectrometer coupled with a multireflection White cell was used to record the IR spectra of transient species. The laser beam, of wavelength 248 nm, passed through the White cell and was reflected six times with two external mirrors so as to photodissociate a flowing mixture of CH$_2$I$_2$ in N$_2$O$_2$ and thereby produced CH$_2$I that subsequently reacted with O$_2$ to form CH$_2$OO. The derivation of conventional time-resolved difference absorption spectra from the temporal profiles recorded at each scan step has been established (20, 25).

The partial IR absorption spectrum (800 to 1500 cm$^{-1}$) of the flowing mixture of CH$_2$I$_2$/N$_2$/O$_2$ (1/20/760, 94 torr) at 340 K (Fig. 2A) exhibits absorption lines of CH$_2$I$_2$ near 1229, 1188, and 1113 cm$^{-1}$. Upon irradiation with light at 248 nm, the absorption of CH$_2$I$_2$ decreased owing to photolysis, whereas new bands near 1435, 1286, 908, and 848 cm$^{-1}$ appeared, as shown in the difference spectrum recorded at 0- to 12.5-μs delays (Fig. 2B); a band with a weak Q-branch near 1241 cm$^{-1}$ (indicated by an arrow) might belong to the same group but is interfered with by absorption of parent or other products. The intensities of these new lines decreased rapidly with time and diminished after ~100 μs; a spectrum recorded 50 to 62.5 μs after photo-irradiation is shown in Fig. 2C. The decay of CH$_2$OO resulted in increased absorption of H$_2$CO.

Because photolysis of CH$_2$I$_2$ produces mainly the CH$_2$I radical (26) and because this radical reacts readily with excess O$_2$ in the system (27, 28), the possible carriers of the observed new bands include CH$_2$IOO and isomers of CH$_2$O$_2$. Most pre-
vious experimental attempts to generate and detect CH₂OO used either the reaction of CH₂ + O₂ or CH₃H + O₃, but the large exothermicity of these reactions makes the stabilization of CH₂OO difficult. In contrast, in the reaction of CH₂ + O₂ → CH₂ + O₂ + I chosen here, the stabilization of CH₂OO is possible because of the small exothermicity of ~13 kJ mol⁻¹.

The observed vibrational wave numbers and relative intensities are compared with theoretical predictions for CH₂OO in Table 1. Previous investigations (12, 18) reported only harmonic vibrational frequencies, so we performed new calculations in order to derive the anharmonic frequencies. The potentially zwitterionic character of the CH₂OO molecule requires appropriate multireference treatment. The harmonic and anharmonic vibrational frequencies have been computed by using a quadratic force field obtained with the n-electron valence state perturbation theory (NEVPT2) method (29) implemented in the Molpro quantum chemistry package (30) by using the CASSCF(8,8) reference wave function. No symmetry has been used in these calculations so as to avoid numerical problems. The anharmonic frequencies (31) have only approximate character because the effects of three- and four-mode couplings have been neglected owing to high computational complexity. Nevertheless, the computed NEVPT2/aVDZ anharmonic frequencies correspond well to the observed experimental bands.

The IR spectra of CH₂OO, dioxirane, methylenebis(oxy), and cis-CH₂JOO simulated according to the geometries and anharmonic vibrational frequencies that were predicted with quantum-chemical calculations are shown in Fig. 2, D to G, respectively. A compilation of anharmonic vibrational levels and IR intensities for the isomers of CH₂OO and other possible intermediate structures used in the simulations is given in tables S1 and S2. The rotational constants used in the simulation are compiled in table S3. For CH₂JOO and CH₂OO, the characteristic OO-stretching modes have wave numbers near 900 cm⁻¹. For dioxirane, two intense features near 1238 and 911 cm⁻¹ are characteristic of symmetric and antisymmetric CO-stretching modes (1/7). For methylenebis(oxy), only an anharmonic NEVPT2 (2,2) stick spectrum is shown because the B3LYP (Becke, three-parameter, Lee-Yang-Parr) rotational constants for each fundamental mode could not be assessed (supplementary text). A comparison of the observed new spectral features with these simulated spectra indicates that the best agreement in terms of relative intensities and positions is obtained for the predicted spectrum of CH₂OO. The Criegee intermediate is predicted to have intense lines at 1458 (52), 1302 (100), 1220 (33), 892 (100), and 853 (31) cm⁻¹; the relative IR intensities are listed in parentheses. The observed features at 1435 (33), 1286 (42), 1241 (39), 908 (100), and 848 (24) cm⁻¹, with typical deviations of 5 to 23 cm⁻¹ from predicted anharmonic vibrational wave numbers. The predicted spectra of other candidate species disagree with the observed spectrum. For example, although dioxirane is predicted to have two intense lines near 1238 and 911 cm⁻¹, near the observed features at 1286 and 848 cm⁻¹, the relative intensities and the rotational contours do not match. The widths of the rotational contours of bands of CH₂JOO are predicted to be much smaller than the observed widths because the massive I atom induces small rotational parameters; the possibility that the observed new features are due to CH₂JOO is positively eliminated. In contrast, the predicted rotational contours of each vibrational band of CH₂OO agree well with observations, except for a weak Q-band near 1241 cm⁻¹ that might experience interference from absorption of the precursor or other product. A comparison of observed and simulated rotational contours for the v₆ and v₅ modes is shown in Fig. 3; those for the v₁ and v₃ modes are shown in figs. S1 and S2, respectively. Most bands of CH₂OO have a mixed a₁a₁-type contour with P-, Q-, and R-branches, whereas the out-of-plane CH₂-wagging (v₆) mode near 848 cm⁻¹

Fig. 2. Comparison of observed spectra with simulated spectra of possible species. (A) IR absorption spectrum of a flowing mixture of CH₂J/N₂/O₂(1/20/760, 94 torr) before photolysis. (B) Difference spectra recorded 0 to 12.5 μs and (C) 50 to 62.5 μs after irradiation of the sample at 248 nm; the spectrum at 300 to 312.5 μs was subtracted for background correction. IR spectra of (D) CH₂OO, (E) dioxirane, (F) methylenebis(oxy), and (G) cis-CH₂JOO were simulated by using the predicted rotational constants, vibrational frequencies, and IR intensities listed in tables S1 and S3.

Table 1. Comparison of experimentally observed wave numbers (per centimeter) and intensities with the vibrational wave numbers (per centimeter) and IR intensities of CH₂OO predicted with various methods.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Sym.</th>
<th>Experiment</th>
<th>Harmonic</th>
<th>Anharmonic</th>
<th>CAS(14,12)</th>
<th>CCSD(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₁</td>
<td>A'</td>
<td>3370</td>
<td>3149 (5)</td>
<td>3215</td>
<td>3290</td>
<td>a-CH str.</td>
</tr>
<tr>
<td>v₂</td>
<td>A'</td>
<td>3197</td>
<td>3030 (1)</td>
<td>3065</td>
<td>3137</td>
<td>s-CH str.</td>
</tr>
<tr>
<td>v₃</td>
<td>A'</td>
<td>1435 (33)</td>
<td>1500</td>
<td>1458 (52)</td>
<td>1465</td>
<td>1483</td>
</tr>
<tr>
<td>v₄</td>
<td>A'</td>
<td>1286 (42)</td>
<td>1338</td>
<td>1302 (100)</td>
<td>1269</td>
<td>1306</td>
</tr>
<tr>
<td>v₅</td>
<td>A'</td>
<td>1241 (39)</td>
<td>1235</td>
<td>1220 (33)</td>
<td>1233</td>
<td>1231</td>
</tr>
<tr>
<td>v₆</td>
<td>A'</td>
<td>908 (100)</td>
<td>916</td>
<td>892 (100)</td>
<td>849</td>
<td>935</td>
</tr>
<tr>
<td>v₇</td>
<td>A'</td>
<td>536</td>
<td>530 (1)</td>
<td>537</td>
<td>529</td>
<td>COO deform</td>
</tr>
<tr>
<td>v₈</td>
<td>A'</td>
<td>848 (24)</td>
<td>856</td>
<td>853 (31)</td>
<td>793</td>
<td>862</td>
</tr>
<tr>
<td>v₉</td>
<td>A'</td>
<td>620</td>
<td>606 (2)</td>
<td>618</td>
<td>632</td>
<td>CH₂ twist</td>
</tr>
</tbody>
</table>

Reference This work This work This work (18) (12)

†Approximate mode description. a, asymmetric; s, symmetric; str., stretch. ‡Relative IR intensities are normalized to the most intense line (v₃) with intensity 124 km mol⁻¹. ‡Integrated IR intensities relative to v₆ are listed in parentheses.
has a characteristic c-type structure with a prominent Q-branch because the dipole moment oscillates mainly along the c axis (perpendicular to the molecular plane) upon vibrational excitation. This unique c-type feature of a planar molecule near 848 cm\(^{-1}\) further supports the assignment of the observed features to CH\(_2\)OO.

The observed wave number of the OO-stretching mode of CH\(_2\)OO near 908 cm\(^{-1}\) is much smaller than that of the corresponding modes of CH\(_3\)OO at 1117 cm\(^{-1}\) (2f), CH\(_3\)C(O)OO (32) at 1102 cm\(^{-1}\), and CH\(_2\)HC(O)OO at 1108 cm\(^{-1}\) (33) determined with a similar technique. The observed wave number of the CO-stretching mode near 1286 cm\(^{-1}\) is much larger than that of the corresponding mode of CH\(_3\)OO at 902 cm\(^{-1}\) (34) observed in a matrix, indicating some double-bond character. These trends strongly support a zwiterionic, rather than singlet biradical, structural description of CH\(_2\)OO because of a strengthened C–O bond and a weakened O–O bond.

The ~50-μs lifetime of CH\(_2\)OO observed in our experiment is much shorter than that (~2 ms) reported by Welz et al. (11), who used [CH\(_2\)I\(_2\)]\(_0\) ∼9×10\(^{11}\) molecules cm\(^{-3}\) in their experiments. Because the sensitivity of IR absorption is not as good as that of mass detection, a higher concentration of [CH\(_2\)I\(_2\)]\(_0\) ∼4×10\(^{13}\) molecules cm\(^{-3}\) is needed in our experiments in order to record a satisfactory spectrum of CH\(_2\)OO. In some preliminary low-resolution experiments, we varied [CH\(_2\)I\(_2\)] from 1.0 × 10\(^{-3}\) to 2.8 × 10\(^{-4}\) molecules cm\(^{-3}\) and found that the lifetime of CH\(_2\)OO decreased from ~150 to 15 μs, indicating that the bimolecular reaction—either CH\(_2\)OO + I \rightarrow CH\(_3\)O + HI or CH\(_3\)O + CH\(_3\)I—might be responsible for this rapid decay. More detailed kinetic measurements are in progress.

With our detection method, we can probe CH\(_2\)OO directly in a reaction. The advantage is demonstrated in the investigation of the yield of CH\(_2\)OO from the reaction CH\(_3\)I + O \(_2\). Solar photolysis of CH\(_3\)I, one major source of iodine in the marine boundary layer, generates CH\(_3\)I and I. The reaction of CH\(_3\)I + O \(_2\) is important in the atmosphere partly because this reaction releases the second I atom to form IO, which can affect O\(_3\), HO\(_2\), and NO\(_x\) levels and also lead to the formation of particulates in the atmosphere (35). Huang et al. detected I atom as a product of the reaction of CH\(_3\)I with O \(_2\) by probing the IR absorption of I atom at 7603.138 cm\(^{-1}\). These authors reported that O\(_2\) stabilizes CH\(_2\)I\(_2\)OO with remarkable efficiency (13 times that of N\(_2\)), hence decreasing the yield of I atoms (28). The yield of CH\(_2\)OO from CH\(_3\)I + O \(_2\) was estimated to be 0.04 in air at 760 torr because CH\(_2\)OO is expected to be readily stabilized. However, because these authors probed only I atoms, their measurements could not distinguish between the stabilization of CH\(_2\)I\(_2\)OO and other secondary reactions. With our new detection method, we can probe CH\(_2\)OO directly to provide direct measurements of the yield of CH\(_2\)OO. Contrary to their predictions, in our experiment with O\(_2\) at 90 torr we observed no CH\(_2\)OO, and the yield of CH\(_2\)OO was estimated to be at least 3.5% of CH\(_3\)I with the assumption that the predicted IR intensities of CH\(_2\)OO are correct. Whether this discrepancy is due to the difference in photolysis wavelengths [335 nm in experiments of Huang et al. (28) and 248 nm in this work] — in which the total available energy of CH\(_3\)I \(^{-1}\) (118 and 263 kJ mol\(^{-1}\), respectively) might affect the efficiency of stabilization of CH\(_2\)I\(_2\)OO and CH\(_2\)OO produced from CH\(_3\)I + O \(_2\) — requires further investigation.

**References and Notes**

25. Materials and methods are available as supplementary materials on Science Online.

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**Supplementary Materials**

www.sciencemag.org/cgi/content/full/340/6129/174/DC1

Materials and Methods

Supplementary Text

Figs. S1 and S2

Tables S1 to S3

References (36–44)

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