Supplementary Information

Infrared characterization of formation and resonance stabilization of the Criegee intermediate methyl vinyl ketone oxide

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Table of Contents
Supplementary Note 1. Computational Results ------------------------------------------------------------- 1
Supplementary Note 2. IR spectra of precursor (Z)-(CH₂I)HC=C(CH₃)I (1) ------------------------------- 1
Supplementary Note 3. IR spectra of the iodoalkenyl radical (Z)-C₂H₃C(CH₂)I (2) ------------------- 2
Supplementary Note 4. Photolysis of (Z)-(CH₂I)HC=C(CH₃)I (1) in O₂ at 35 Torr --------------------- 3
Supplementary Note 5. Spectral simulation of conformers of MVKO ------------------------------- 5
Supplementary Note 6. Photolysis of (Z)-(CH₂I)HC=C(CH₃)I in O₂ at high pressure -------------- 5
Supplementary Note 7. Temporal profiles of C₂H₅C(CH₃)I, C₂H₅C(CH₃)OO, and C₂H₅C(CH₃)IOO ------------------------------- 6
Supplementary Note 8. Estimated relative yields of MVKO (3) and C₂H₅C(CH₃)IOO (4) -- 8
Supplementary Table 1. Cartesian coordinates of optimized geometries of precursors (Z)- and (E)- (CH₂I)HC=C(CH₃)I and iodoalkyl radicals (Z)- and (E)-C₂H₃C(CH₃)I and (Z)- and (E)- (CH₂I)CHC(CH₃) predicted with the B3LYP/aug-cc-pVTZ-pp method ------------------------------------------ 10
Supplementary Table 2. Cartesian coordinates of optimized geometries of four conformers of the Criegee intermediates syn-trans-, syn-cis-, anti-trans-, and anti-cis-C₂H₅C(CH₃)OO and dioxole predicted with the B3LYP/aug-cc-pVTZ method ------------------------------------------ 11
Supplementary Table 3. Cartesian coordinates of optimized geometries of nine conformers of iodoperoxy radical C₂H₅C(CH₃)IOO predicted with the B3LYP/aug-cc-pVTZ-pp method---------------------------------- 12
Supplementary Table 4. Cartesian coordinates of optimized geometries of six conformers of iodoperoxy radical C(CH₃)ICHCH₂OO predicted with the B3LYP/aug-cc-pVTZ-pp method ---- 14
Supplementary Table 5. Comparison of experimental vibrational wavenumbers and IR intensities of (Z)- (CH₂I)HC=C(CH₃)I (1) with those of (Z)- and (E)-(CH₂I)HC=C(CH₃)I predicted with the B3LYP/aug-cc-pVTZ-pp method------------------------------------------ 15
Supplementary Table 6. Vibrational wavenumbers and IR intensities of (Z)- and (E)-C₂H₅CC(CH₃)I and (Z)- and (E)-(CH₂I)CHC(CH₃) predicted with the B3LYP/aug-cc-pVTZ-pp method ------------------------------------------ 16
Supplementary Table 7. Vibrational wavenumbers and IR intensities of four conformers of Criegee intermediates C₂H₅C(CH₃)OO and dioxole predicted with the B3LYP/aug-cc-pVTZ method ------------------------------------------ 18
Supplementary Table 8. Vibrational wavenumbers and IR intensities of nine conformers of iodoperoxy radical C₂H₅C(CH₃)IOO predicted with the B3LYP/aug-cc-pVTZ-pp method------ 21
Supplementary Table 9. Vibrational wavenumbers and IR intensities of six conformers of iodoperoxy radical C(CH₃)ICHCH₂OO predicted with the B3LYP/aug-cc-pVTZ-pp method ---- 24
Supplementary Table 10. Rotational parameters and type ratios for each vibrational state of four conformers of Criegee intermediates MKVO predicted with the B3LYP/aug-cc-pVTZ method ------------------------------------------ 26
Supplementary Table 11. Comparison of observed vibrational wavenumbers of (Z)-C_2H_3C(CH_3)I (2) in region 800–1450 cm\(^{-1}\) with those calculated with the B3LYP/aug-cc-pVTZ-pp method.-----------------------------------------------28

Supplementary Table 12. Comparison of observed vibrational wavenumbers of syn-trans-C_2H_3C(CH_3)OO (3) in region 800–1500 cm\(^{-1}\) with those calculated with the B3LYP/aug-cc-pVTZ method.-----------------------------------------------29

Supplementary Table 13. Comparison of observed vibrational wavenumbers of syn-cis-C_2H_3C(CH_3)OO in region 800–1500 cm\(^{-1}\) with those calculated with the B3LYP/aug-cc-pVTZ method.-----------------------------------------------30

Supplementary Table 14. Comparison of observed vibrational wavenumbers of C_2H_3C(CH_3)IOO (4) in region 800–1500 cm\(^{-1}\) with C_2H_3C(CH_3)IOO-1 and C_2H_3C(CH_3)IOO-2 calculated with the B3LYP/aug-cc-pVTZ-pp method.-----------------------------------------------31

Supplementary Table 15. Summary on estimates of concentrations of species in varied experiments.------------------------------------------------------------------------------------------------------------------------32

Supplementary Figure 1. Geometries of conformers of methyl vinyl ketone oxide (MVKO) and dioxole predicted with the B3LYP/aug-cc-pVTZ method.-----------------------------------------------33

Supplementary Figure 2. Geometries of precursors (Z)-(E)-(CH_2)IHC=C(CH_3)I and (Z)/(E)-iodoalkyl radicals C_2H_3C(CH_3)I and (CH_2)IHC(CH_3) predicted with the B3LYP/aug-cc-pVTZ-pp method.-----------------------------------------------34

Supplementary Figure 3. Geometries of nine conformers of iodoperoxy radicals C_2H_3C(CH_3)IO predicted with the B3LYP/aug-cc-pVTZ-pp method.-----------------------------------------------35

Supplementary Figure 4. Geometries of six conformers of iodoperoxy radicals C(CH_3)ICCHCH_2OO predicted with the B3LYP/aug-cc-pVTZ-pp method.-----------------------------------------------36

Supplementary Figure 5. Comparison of IR spectra of (Z)-CH_2IHC=C(CH_3)I (1) in the gaseous phase and in solid p-H_2 with quantum-chemical calculations.-----------------------------------------------37

Supplementary Figure 6. Temporal evolution of observed spectra and processed spectra in region 1450–850 cm\(^{-1}\) at resolution 1.0 cm\(^{-1}\) upon photolysis at 248 nm of a flowing mixture of (Z)-1,3-diiodo-but-2-ene/N_2 (0.03/75 Torr) and comparison with predicted stick spectra.--------------------------38

Supplementary Figure 7. Comparison of IR spectra of (Z)-C_2H_3C(CH_3)I (2) in the gaseous phase with quantum-chemical calculations.-------------------------------------------------------------------------------------------------39

Supplementary Figure 8. Temporal evolution of observed and processed spectra in region 1450–850 cm\(^{-1}\) at resolution 0.5 cm\(^{-1}\) upon photolysis at 248 nm of a flowing mixture of (Z)-1,3-diiodo-but-2-ene/O_2 (0.04/35 Torr).---------------------------------------------------------------------------------------------40

Supplementary Figure 9. Resonance structures and frontier orbitals of syn-trans-MVKO.-----------------------------------------------41

Supplementary Figure 10. Temporal evolution of observed and processed spectra in region 1450–850 cm\(^{-1}\) at resolution 1.0 cm\(^{-1}\) upon photolysis at 248 nm of a flowing mixture of (Z)-1,3-diiodo-but-2-ene/O_2 (0.042/347 Torr) ____________________________________________42
Supplementary Figure 11. Temporal evolution of observed and processed spectra in region 1450–850 cm⁻¹ at resolution 1.0 cm⁻¹ upon photolysis at 248 nm of a flowing mixture of (Z)-1,3-diiodo-but-2-ene/O₂ (0.035/236 Torr) 43

Supplementary Figure 12. Comparison of bands in group C with stick IR spectra of nine conformers of iodoperoxy radical C₂H₃C(CH₃)IOO 44

Supplementary Figure 13. Comparison of bands in group C with stick IR spectra of six conformers of iodoperoxy radical C(CH₃)ICHCH₂OO 45

Supplementary Figure 14. Temporal profiles of species upon photolysis at 248 nm of a mixture of (Z)-(CH₂I)HC=C(CH₃)I (0.04 Torr) and O₂ (35 Torr) and a mixture of (Z)-(CH₂I)HC=C(CH₃)I (0.04 Torr) and O₂ (347 Torr). 46

Supplementary References 47
**Supplementary Note 1. Computational Results**

The geometries and relative energies of four conformers of Criegee intermediates \( \text{syn-trans-} \), \( \text{syn-cis-} \), \( \text{anti-trans-} \), and \( \text{anti-cis-} \)-C\(_2\)H\(_3\)C(CH\(_3\))OO and dioxole are presented in Supplementary Figure 1. Those of precursors (\( Z \))- and (\( E \))-(CH\(_2\))IHC=C(CH\(_3\))I and iodoalkyl radicals (\( Z \))- and (\( E \))-conformers of C\(_2\)H\(_2\)C(CH\(_3\))I and (CH\(_2\))CHC(CH\(_3\)) are presented in Supplementary Figure 2. The geometries and relative energies of nine possible conformers of iodoperoxy radical C\(_2\)H\(_3\)C(CH\(_3\))IOO and six possible conformers of C(CH\(_3\))ICHCH\(_2\)OO are presented in Supplementary Figures 3 and 4, respectively. Cartesian coordinates of all conformers of (CH\(_2\))IHC=C(CH\(_3\))I, C\(_2\)H\(_3\)C(CH\(_3\))I, (CH\(_2\))CHC(CH\(_3\)), C\(_2\)H\(_3\)C(CH\(_3\))OO, dioxole, C\(_2\)H\(_3\)C(CH\(_3\))IOO, and C(CH\(_3\))ICHCH\(_2\)OO are listed in Supplementary Tables 1–4.

Computed scaled harmonic vibrational wavenumbers and IR intensities of precursors (\( Z \))- and (\( E \))-(CH\(_2\))IHC=C(CH\(_3\))I, iodoalkyl radicals (\( Z \))- and (\( E \))-conformers of C\(_2\)H\(_2\)C(CH\(_3\))I and (CH\(_2\))CHC(CH\(_3\)), Criegee intermediates \( \text{syn-trans-} \), \( \text{syn-cis-} \), \( \text{anti-trans-} \), and \( \text{anti-cis-} \)-C\(_2\)H\(_3\)C(CH\(_3\))OO and dioxole, nine conformers of iodoperoxy radicals C\(_2\)H\(_3\)C(CH\(_3\))IOO, and six conformers of iodoperoxy radicals C(CH\(_3\))ICHCH\(_2\)OO are listed in Supplementary Tables 5–9, respectively. The anharmonic vibrational wavenumbers of Criegee intermediates \( \text{syn-trans-} \), \( \text{syn-cis-} \), \( \text{anti-trans-} \), and \( \text{anti-cis-} \)-C\(_2\)H\(_3\)C(CH\(_3\))OO and dioxole are also listed in Supplementary Table 7. The rotational parameters and type ratios for each vibrational state of the four conformers of Criegee intermediates MKVO are listed in Supplementary Table 10.

**Supplementary Note 2. IR spectra of precursor (\( Z \))-(CH\(_2\))IHC=C(CH\(_3\))I (1)**

The IR spectrum of gaseous precursor (\( Z \))-(CH\(_2\))IHC=C(CH\(_3\))I (1) in region 1450–850 cm\(^{-1}\) is presented in Supplementary Figure 5(a). This spectrum is compared with the spectrum of (1) in a solid \( p \)-H\(_2\) matrix\(^1\) and stick spectra of (1) predicted with the B2PLYP-D3 and B3LYP methods in
Supplementary Figure 5. Four intense bands near 1434, 1294, 1152, and 1063 cm\(^{-1}\) and two weaker ones near 1384 and 1169 cm\(^{-1}\) (the latter appears as a shoulder of the band near 1152 cm\(^{-1}\)) were observed, in agreement with those observed for the same conformer in a \(p\)-H\(_2\) matrix at 3.2 K.\(^{1}\)

According to the plot of experimental wavenumbers versus harmonic vibrational wavenumbers of (I) predicted with the B3LYP/aug-cc-pVTZ-pp method, we derived a linear scaling equation \(y = (0.9708 \pm 0.0159) x + (9.3 \pm 20.7)\), in which \(y\) and \(x\) are experimental and harmonic vibrational wavenumbers, respectively. All observed wavenumbers and intensities are compared with those observed in solid \(p\)-H\(_2\) and scaled harmonic vibrational wavenumbers and IR intensities in Supplementary Tables 5. We employed this equation to scale the predicted harmonic vibrational wavenumbers of other species considered in this work. On comparison of the spectrum of precursor reported by Barber et al. (in Supporting Information),\(^{2}\) the samples that these authors used were clearly a mixture of both (Z)- and (E)-conformers, with the former dominant, as they stated. In this work, a nearly pure (Z)-conformer (I) was used.

**Supplementary Note 3. IR spectra of the iodoalkenyl radical (Z)-C\(_2\)H\(_3\)C(CH\(_3\))I (2)**

When the diiodoalkene precursor (I) in N\(_2\) was irradiated with light at 248 nm, the intensity of its lines decreased significantly, as shown in Supplementary Figure 6(b) as a difference spectrum obtained from the \(ac\)-channel recorded 0–3 \(\mu\)s after irradiation; intense negative bands indicate the destruction of the precursor, whereas the formation of products is indicated by some extremely weak positive features. The expanded spectra of products recorded 0–3 and 10–15 \(\mu\)s after irradiation are shown in Supplementary Figures S6(c) and S6(d), respectively, with the negative bands truncated. The features corresponding to the primary photolysis product decreased with time, but a broad feature near 915 cm\(^{-1}\) and two sharp lines at 919 and 892 cm\(^{-1}\) increased continuously. We termed these six features near 1406, 1261, 1109, 1019, 925, and 873 cm\(^{-1}\) that are associated with the primary photolysis product as group A and marked them A\(_1\)–A\(_6\) in Supplementary Figure 6(c); the
bands with positions near 925 and 873 cm\(^{-1}\) are less certain because of their small intensities and severe interference from the broad feature near 915 cm\(^{-1}\). The intensities of these features in group A decreased significantly in the spectrum recorded 10–15 \(\mu\)s after irradiation, indicating the transient nature of the carrier. We added the bands of the precursor, Supplementary Figure 6(a), back to the spectrum in Supplementary Figure 6(c) to minimize its interference and present it in Supplementary Figure 6(e); the regions with which the intense absorption of the precursor might interfere are shaded with grey. Some regions of the parent absorption could not be compensated completely because some precursors might become internally excited upon irradiation, so that their absorption spectrum is differed from that before irradiation.

The assignments of these new features in group A to the iodoalkenyl radical \((Z)-C_2H_3C(CH_3)I\) (2) is discussed in the main text. Comparison of IR spectra of features in group with the IR stick spectra of two possible photolysis products, \((Z)-C_2H_3C(CH_3)I\) (2) and \((Z)-(CH_2I)CHC(CH_3)_3\), according to the scaled harmonic vibrational wavenumbers predicted with the B3LYP method are shown in Figure 2. The observed new features agree satisfactorily with lines predicted near 1418, 1261, 1108, 930, and 887 cm\(^{-1}\) for (2), as compared in Supplementary Table 11. Comparison of IR spectra of lines in group A with the IR stick spectra of \((Z)-C_2H_3C(CH_3)I\) (2) and \((E)-C_2H_3C(CH_3)I\) is presented in Supplementary Figure 7; the agreement of experiments with the latter is poor, indicating that the conversion from \((Z)-\) to \((E)-\)conformation did not occur.

**Supplementary Note 4. Photolysis of \((Z)-(CH_2I)HC=C(CH_3)I\) (1) in O\(_2\) at 35 Torr**

The top trace in Supplementary Figure 8(a) shows the absorption spectrum, on a reduced scale, of a flowing mixture of (1) (0.04 Torr) and O\(_2\) (35 Torr) before photolysis; Supplementary Figures 8(a)–(c) show expanded difference spectra recorded 0–5, 5–10, and 30–35 \(\mu\)s, respectively, after photolysis of the mixture at 248 nm; the negative bands corresponding to the destruction of the
precursor are truncated. The spectrum of the iodoalkenyl radical \((Z)-C_2H_3C(CH_3)I\) (2) shown in Supplementary Figure 6(e) is reproduced in Supplementary Figure 8(d) for comparison. Small bands of (2) were observed only 0–5 µs after irradiation before it reacted completely with \(O_2\). Some new features appeared and their intensities reached maxima near 5–10 µs, whereas some bands appeared at a later period and became more prominent in the spectrum recorded 30–35 µs after irradiation; the latter features correspond to absorption of the end product methyl vinyl ketone (MVK, \(C_2H_3C(O)CH_3\)), of which spectrum is presented in Supplementary Figure 8(e) for comparison. We stripped absorption bands of the iodoalkenyl radical (2) and MVK and added back the bands of the precursor (1) in spectra shown in Supplementary Figures 8(a)–(c); the resultant spectra are presented in Supplementary Figures 8(f)–(h). Seven bands near 1416, 1383, 1346, 1060, 987, 948, and 916/908 cm\(^{-1}\) that have correlated variations in intensity and reached their maxima 5–10 µs after irradiation are termed group B and marked \(B_1–B_7\) in Supplementary Figure 8(g); feature \(B_7\) contains two sharp bands at 916 and 908 cm\(^{-1}\). The regions with which intense absorption of the precursor might interfere are shaded with grey; however, perhaps only the region 1140–1180 cm\(^{-1}\) containing the most intense absorption band of the precursor is unreliable. Although feature \(B_4\) near 1060 cm\(^{-1}\) overlaps partially with the absorption band of the precursor near 1063 cm\(^{-1}\), its absorption contour is expected to be reliable because of the excellent reproducibility of our FTIR spectra. The weak band near 891 cm\(^{-1}\) does not belong to group B because of its unsatisfactory correlation in intensity variations in varied reaction periods. These features in group B are assigned to the Criegee intermediate syn-trans-MVKO (3), as discussed in the main text. Comparison of observed vibrational wavenumbers of syn-trans-\(C_2H_3C(CH_3)OO\) (3) in region 800–1500 cm\(^{-1}\) with those calculated with the B3LYP/aug-cc-pVTZ method is shown in Supplementary Table 12. The major resonance structures of syn-trans-MVKO (3) is shown in Supplementary Figure 9.

Some weak features might be tentatively assigned to syn-cis-\(C_2H_3C(CH_3)OO\), as discussed in
the main text. Observed vibrational wavenumbers of syn-ciss-C\(_2\)H\(_3\)C(CH\(_3\))OO in region 800–1500 cm\(^{-1}\) are compared with those predicted with the B3LYP/aug-cc-pVTZ method in Supplementary Table 13.

**Supplementary Note 5. Spectral simulation of conformers of MVKO**

With program PGopher,\(^3\) we simulated the rotational contours of some vibrational modes of Criegee intermediates syn-trans-, syn-cis-, anti-trans-, and anti-cis-MVKO using rotational parameters of the lower state (\(A''\), \(B''\), and \(C''\)) and upper states (\(A', B',\) and \(C'\)), and ratios of \(a\)-type/\(b\)-type/\(c\)-type predicted with the B3LYP/aug-cc-pVTZ method (Supplementary Table 10). The parameters employed in the simulations are \(J_{\text{max}} = 200\), \(T = 298\) K, Gaussian width (FWHM) = 0.64 (corresponding to the instrument resolution of 0.5 cm\(^{-1}\)). The weighting factors of bands of types \(a\), \(b\), and \(c\) in each resultant vibrational absorption band were determined by the squares of the projections of the dipole derivatives for each vibrational mode onto rotational axes \(a\), \(b\) and \(c\).

**Supplementary Note 6. Photolysis of (Z)-(CH\(_2\))IHC=C(CH\(_3\))I in O\(_2\) at high pressure**

The top trace in Supplementary Figure 10(a) shows the absorption spectrum, on a reduced scale, of (Z)-1,3-diiodobut-2-ene/O\(_2\) (0.042/347 Torr) in a flowing mixture before photolysis. Supplementary Figures 10(a)–(c) present the difference absorption spectra of this flowing mixture 0–25, 25–50, and 50–100 \(\mu\)s after photolysis; the spectra were recorded with the internal 24-bit ADC with temporal resolution 12.5 \(\mu\)s. Supplementary Figures 10(d) and 10(e) depict reference spectra of syn-trans-MVKO (3) and MVK, respectively. Supplementary Figures 10(f)–(h) show the spectra processed from Supplementary Figures 10(a)–10(c), with absorption of MVKO (3) and MVK stripped and that of the precursor (1) added back. Similar plots for experiments of (Z)-1,3-diiodobut-2-ene/O\(_2\) (0.035/236 Torr) 0–10, 10–20, and 20–30 \(\mu\)s after photolysis, recorded with an external ADC, and those processed with bands of MVKO (3) and MVK removed and those of the precursor
(1) added back are presented in Supplementary Figure 11. Six bands near 1375, 1213, 1108, 1063, 986, and 885 cm\(^{-1}\) that showed correlated intensity variations and decayed slowly after irradiation are termed group C and marked C\(_1\)–C\(_6\) in Supplementary Figures 10(f) and 11(f). The band near 934 cm\(^{-1}\) appears not to be associated with group C because of its unsatisfactory correlation in intensity variations at varied experimental period; it might be an artifact from stripping the most-intense band of syn-trans-MVKO (3). The observed spectra of bands of group C are compared with the stick IR spectra of nine possible conformers of C\(_2\)H\(_3\)C(CH\(_3\))IOO (4) in Supplementary Figure 12 and with the stick spectra of six possible conformers of C(CH\(_3\))ICHCH\(_2\)OO in Supplementary Figure 13. These features in group C are assigned to the iodoperoxy adduct C\(_2\)H\(_3\)C(CH\(_3\))IOO (4), as discussed in the main text. Comparison of observed vibrational wavenumbers of C\(_2\)H\(_3\)C(CH\(_3\))IOO (4) in region 800–1500 cm\(^{-1}\) with those calculated with the B3LYP/aug-cc-pVTZ method for the two least-energy conformers is shown in Supplementary Table 14.

**Supplementary Note 7. Temporal profiles of C\(_2\)H\(_3\)C(CH\(_3\))I (2), C\(_2\)H\(_3\)C(CH\(_3\))OO (3), and C\(_2\)H\(_3\)C(CH\(_3\))IOO (4)**

Supplementary Figure 14(a) presents temporal profiles of the iodoalkenyl radical (2) (black triangles) and the MVKO (3) (blue circles) upon UV irradiation of (1) in O\(_2\) at 35 Torr. Parts of band A\(_2\) (1260–1270 cm\(^{-1}\)) and B\(_6\) (920–960 cm\(^{-1}\)) in the raw spectra were integrated to yield the temporal evolution of (2) and (3), respectively. The integrated intensity of the iodoalkenyl radical (2) showed an immediate rise upon UV irradiation of the mixture, followed by a rapid decay before it reached a non-zero baseline. The non-zero baseline is due to some contribution of the final product MVK shown in Supplementary Figure S8(e), which was unavoidable. The integrated intensity of MVKO (3) showed an initial rise from zero, followed by a slow decay; its rate of rise correlates well with the rate of decay of (2), supporting that (3) was produced from the reaction of (2) with O\(_2\) and that our
spectral assignments are reasonable.

Supplementary Figure 14(b) presents the temporal profiles of iodoperoxy adduct (4) (black triangles and red inverted triangles) and MVKO (3) (blue circles) in an experiment of (1) in O\textsubscript{2} at 347 Torr. Parts of bands C\textsubscript{3} (1100–1120 cm\textsuperscript{-1}), C\textsubscript{6} (862–907 cm\textsuperscript{-1}), and B\textsubscript{6} (920–960 cm\textsuperscript{-1}) were integrated to yield the temporal evolution of (4) and (3), respectively. All profiles were normalized for ease of comparison; species (3) and (4) showed a similarly sharp rise due to the rapid formation reaction of (2) with O\textsubscript{2} at high pressure, followed by different slow decays. The similar rate of rise is consistent with the expectation from a parallel reaction, supporting that MVKO (3) and the iodoperoxy adduct (4) were produced from the same reaction, that of iodoalkenyl radical (2) with O\textsubscript{2}. In contrast, the temporal profile of MVK (pink diamonds, integrated over 1250–1270 cm\textsuperscript{-1}) had a slow rise, indicating the nature of secondary formation. The fraction of loss of MVKO (3) appeared to be smaller than that of (4). This might be because band B\textsubscript{6} overlaps with an intense band of MVK in this region, and MVK is a major product when O\textsubscript{2} pressure is high. The profile of (3) after 0.2 ms is thus unreliable and might reflect mostly the behavior of MVK. Further experiments with higher spectral resolution are needed to clarify this problem.

The spectra obtained at 35 Torr showed predominant production of (3) with little contribution of (4) (Supplementary Figure 8). In contrast, at 236 and 347 Torr, the yield of (3) decreased and that of (4) increased significantly (Supplementary Figures 10 and 11). The analysis is listed in Supplementary Table 15 and discussed in the following section. This observation is also consistent with the expectation that the iodoperoxy adduct (4) is stabilized at higher pressure instead of decomposition to MVKO + I, similarly to what was observed in experiments of CH\textsubscript{2}I + O\textsubscript{2}\textsuperscript{4}. Lin et al. recently proposed that, based on their observation of the temporal profiles of UV absorption of MVKO (3) above 50 Torr, the iodoperoxy adduct was produced from the source reaction but decomposed to MVKO + I at a time scale of ms\textsuperscript{5} in support of our observation of (4). We did
observe the decay of iodoperoxy adduct, but we are uncertain about the formation of MVKO (3) from (4) because the interference from the intense band of MVK, as stated previously.

Supplementary Note 8. Estimated relative yields of MVKO (3) and C₂H₃C(CH₃)IOO (4)

The relative yields of MVKO (3) and (Z)-C₂H₃C(CH₃)IOO (4) at varied pressures were estimated on integrating the destruction of a band (1130–1190 cm⁻¹) of precursor (1), the formation of band B₆ (920–960 cm⁻¹) of MVKO (3) and bands C₃ (1100–1120 cm⁻¹) and C₆ (862–907 cm⁻¹) of C₂H₃C(CH₃)IOO (4); these integrated absorbance were divided with their respective IR intensities predicted with the B3LYP method. The concentration c (in molecule cm⁻³) of each species except (1) in the photolysis region was calculated according to equation (1),

\[
c = 2.65 \times \frac{2.30 \int \Delta A \, dV}{l \times S}
\]

in which 2.65 is the volume ratio, \(V_{IR}/V_{UV}\), for the IR probe and UV photolysis,⁶ \(\int \Delta A \, dv\) is the intensity in cm⁻¹ for the integrated region in the difference spectrum (base 10), 2.30 is \(\ln 10\), \(l\) is 360 cm for IR path length, and \(S\) is the band intensity in cm molecule⁻¹ calculated with the B3LYP method. The partial pressure of (1) was derived on comparing the observed integrated absorbance of IR bands in regions 1130–1190 cm⁻¹ and 1025–1085 cm⁻¹ with the calibration curve obtained at varied pressures. The experimental results are summarized in Supplementary Table S15. We emphasize that the error of the calculated IR intensity might be as large as factor 2 and is not included in the listed errors. Furthermore, as some bands might suffer interference from absorption of other species, the estimated concentrations might have large errors. Nevertheless, a comparison of the relative values of the same species is expected to be reliable.

Because band C₆ of C₂H₃C(CH₃)IOO (4) in region 862–907 cm⁻¹ overlaps with the weak band
B7 of MVKO (3), we performed spectrum subtraction to remove the contribution of (3) and estimated the error associated with this interference to be less than 11%. Even including this possible errors, the observed intensity of band C₆ relative to those of other bands in group C appeared, however, to be much greater than theoretically predicted; the absolute concentration of (4) according to band C₆ might be overestimated. As shown in rows 10 and 11 of Supplementary Table S15, the estimated concentration of (4) according to bands C₃ and C₆ varied by factor 1.5–2.3.

Nevertheless, the percentage variation of concentrations estimated from each band as the total pressure increased, after taking into account the difference in photolysis yield of the precursor (1) in each experiment, is expected to be reliable. The derived relative concentrations of (3) and (4) are compared at varied pressure. From rows 12–14 in Supplementary Table 15, it is clear that the relative yield of MVKO (3) decreased to ~63%, whereas that of the iodoperoxy adduct (4) increased significantly to a factor 1.8–2.9, as the pressure increased from 35 Torr to 347 Torr.
**Supplementary Table 1** Cartesian coordinates of optimized geometries of precursors (Z)- and (E)- (CH$_2$I)HC=C(CH$_3$)$_3$I and iodoalkyl radicals (Z)- and (E)-C$_2$H$_5$C(CH$_3$)$_3$I and (Z)- and (E)- (CH$_2$I)CHC(CH$_3$)$_3$I predicted with the B3LYP/aug-cc-pVTZ-pp method.

|          | x       | y       | z       |          | x       | y       | z       |
|----------|---------|---------|---------|----------|---------|---------|---------|
| (Z)-(CH$_2$I)HC=C(CH$_3$)$_3$I |         |         |         | (E)-(CH$_2$I)HC=C(CH$_3$)$_3$I |         |         |         |
| C$_1$    | -0.86339| 0.34407 | 1.17814 | C$_1$    | -1.32719| -0.66300| 1.12428 |
| C$_2$    | -0.00616| 1.38122 | 0.58527 | C$_2$    | 0.00355 | -0.08842| 0.84376 |
| C$_3$    | 1.21426 | 1.25485 | 0.06672 | C$_3$    | 0.97664 | -0.70146| 0.16870 |
| C$_4$    | 2.01770 | 2.37724 | -0.50570| C$_4$    | 0.95084 | -2.04267| -0.48671|
| H$_1$    | -0.36188| -0.60061| 1.34490 | H$_1$    | -1.68249| -0.41647| 2.11797 |
| H$_2$    | -1.37213| 0.68000 | 2.07420 | H$_2$    | -1.41672| -1.72564| 0.94465 |
| H$_3$    | -0.42431| 2.38418 | 0.56639 | H$_3$    | 0.17318 | 0.90676 | 1.23172 |
| H$_4$    | 2.96739 | 2.49162 | 0.01892 | H$_4$    | 1.14757 | -1.94874| -1.55573|
| H$_5$    | 2.24994 | 2.19618 | -1.55652| H$_5$    | 1.72281 | -2.69406| -0.07434|
| H$_6$    | 1.46150 | 3.31266 | -0.42875| H$_6$    | -0.01543| -2.53002| -0.36326|
| I$_1$    | 2.20124 | -0.63627| -0.02399| I$_1$    | 2.83370 | 0.32656 | -0.05947|
| I$_2$    | -2.55398| -0.16766| -0.16404| I$_2$    | -2.90072| 0.22781 | -0.17075|

|          | x       | y       | z       |          | x       | y       | z       |
|----------|---------|---------|---------|----------|---------|---------|---------|
| (Z)-(C$_2$H$_5$I)C(CH$_3$)$_3$I |         |         |         | (E)-(C$_2$H$_5$I)C(CH$_3$)$_3$I |         |         |         |
| C$_1$    | -2.12400| -1.67023| 0.00000 | C$_1$    | 1.60646 | 2.89572 | 0.00000 |
| C$_2$    | -2.12260| -0.29766| 0.00000 | C$_2$    | 1.28358 | 1.55870 | 0.00000 |
| C$_3$    | -1.05063| 0.58203 | 0.00000 | C$_3$    | 1.02600 | 1.02600 | 0.00000 |
| C$_4$    | -1.18368| 2.06637 | 0.00000 | C$_4$    | 1.78190 | 0.00000 | 0.00000 |
| H$_1$    | -1.20694| -2.24109| 0.00000 | H$_1$    | 2.64163 | 3.20242 | 0.00000 |
| H$_2$    | -3.05594| -2.21494| 0.00000 | H$_2$    | 0.86246 | 3.67838 | 0.00000 |
| H$_3$    | -3.09169| 0.19715 | 0.00000 | H$_3$    | 2.10591 | 0.85388 | 0.00000 |
| H$_4$    | -0.70936| 2.51327 | 0.87730 | H$_4$    | -1.88661| 1.53908 | 0.00000 |
| H$_5$    | -0.70883| 2.51342 | -0.87730| H$_5$    | -1.88661| 1.53908 | 0.87767 |
| H$_6$    | -2.23818| 2.34761 | 0.00000 | H$_6$    | -1.10240| 2.85622 | 0.00000 |
| I$_1$    | 0.94144 | -0.13582| 0.00000 | I$_1$    | -0.19578| -1.08006| 0.00000 |

|          | x       | y       | z       |          | x       | y       | z       |
|----------|---------|---------|---------|----------|---------|---------|---------|
| (Z)-(CH$_2$I)CHC(CH$_3$)$_3$I |         |         |         | (E)-(CH$_2$I)CHC(CH$_3$)$_3$I |         |         |         |
| C$_1$    | -0.49186| 1.12935 | 0.17418 | C$_1$    | 0.64727 | -0.74350| -0.72959|
| C$_2$    | -1.68724| 0.49456 | -0.42624| C$_2$    | 1.65206 | -0.96739| 0.35463 |
| C$_3$    | -2.72293| 0.06829 | 0.25386 | C$_3$    | 2.76830 | -0.29032| 0.46848 |
| C$_4$    | -4.03259| -0.55200| 0.06234 | C$_4$    | 3.52726 | 0.81821 | -0.10869|
| H$_1$    | -0.59465| 1.30843 | 1.23704 | H$_1$    | 0.30367 | -1.66665| -1.18315|
| H$_2$    | -0.17982| 2.02905 | -0.34404| H$_2$    | 0.97040 | -0.04326| -1.48991|
| H$_3$    | -1.68495| 0.39125 | -1.51500| H$_3$    | 1.42376 | -1.76235| 1.05060 |
| H$_4$    | -4.09373| -1.51284| 0.57787 | H$_4$    | 3.68479 | 1.60691 | 0.63031 |
| H$_5$    | -4.83350| 0.08020 | 0.45126 | H$_5$    | 4.51093 | 0.48966 | -0.45053|
| H$_6$    | -4.22958| -0.72806| -1.00389| H$_6$    | 3.00671 | 1.26757 | -0.96493|
| I$_1$    | 1.30611 | -0.15867| 0.00400 | I$_1$    | -1.23528| 0.13596 | 0.04816 |
Supplementary Table 2. Cartesian coordinates of optimized geometries of four conformers of Criegee intermediates syn-trans-, syn-cis-, anti-trans-, and anti-cis-C$_2$H$_3$C(CH$_3$)OO and dioxole predicted with the B3LYP/aug-cc-pVTZ method.

|       | syn-trans- C$_2$H$_3$C(CH$_3$)OO | syn-cis-C$_2$H$_3$C(CH$_3$)OO |
|-------|----------------------------------|---------------------------------|
| C$_1$ | -2.44486                         | 2.28191                         |
| C$_2$ | -1.25774                         | 0.48547                         |
| C$_3$ | 0.02300                          | 0.32295                         |
| C$_4$ | 0.28325                          | 1.44766                         |
| H$_1$ | -2.54373                         | -1.54785                        |
| H$_2$ | -3.36098                         | 0.00000                         |
| H$_3$ | -1.20522                         | 0.00000                         |
| H$_4$ | 0.90061                          | 0.00000                         |
| H$_5$ | 0.90061                          | 0.00000                         |
| H$_6$ | -0.63139                         | -0.49474                        |
| O$_1$ | 1.01810                          | -0.87065                        |
| O$_2$ | 2.27167                          | 0.00000                         |

|       | anti-trans-C$_2$H$_3$C(CH$_3$)OO | anti-cis-C$_2$H$_3$C(CH$_3$)OO |
|-------|----------------------------------|---------------------------------|
| C$_1$ | -2.05395                         | 1.03612                         |
| C$_2$ | -0.71361                         | 1.15505                         |
| C$_3$ | 0.05380                          | 0.10647                         |
| C$_4$ | -0.51097                         | 0.43163                         |
| H$_1$ | -2.64000                         | 0.07046                         |
| H$_2$ | -2.59672                         | 1.93281                         |
| H$_3$ | -0.12962                         | 2.14761                         |
| H$_4$ | -1.13347                         | 1.02574                         |
| H$_5$ | -1.13347                         | -0.87933                        |
| H$_6$ | 0.29635                          | -0.47916                        |
| O$_1$ | 1.34510                          | -1.14998                        |
| O$_2$ | 1.99034                          | 0.61236                         |

|       | dioxole                          |                                |
|-------|----------------------------------|--------------------------------|
| C$_1$ | -2.17104                         | -0.00224                       |
| C$_2$ | -0.68504                         | -0.00172                       |
| C$_3$ | 0.16846                          | -0.01503                       |
| C$_4$ | 1.55813                          | 0.02299                        |
| H$_1$ | -0.08531                         | 0.02460                        |
| H$_2$ | 1.36535                          | -0.3678                        |
| H$_3$ | -2.53256                         | 0.88493                        |
| H$_4$ | -2.58656                         | -0.01377                       |
| H$_5$ | -2.53179                         | -0.87664                       |
| H$_6$ | -0.08485                         | -0.02954                       |
| O$_1$ | 2.09931                          | 0.94487                        |
| O$_2$ | 2.17307                          | -0.83639                       |
Supplementary Table 3. Cartesian coordinates of optimized geometries of nine conformers of iodoperoxy radical C$_2$H$_3$C(CH$_3$)OO predicted with the B3LYP/aug-cc-pVTZ-pp method.

|         | C$_2$H$_3$C(CH$_3$)OO-1 |         | C$_2$H$_3$C(CH$_3$)OO-2 |
|---------|------------------------|---------|------------------------|
| C1      | 2.39257                | -1.89435 | -0.14418               | 2.41424 | -1.74673 | -0.51159 |
| C2      | 1.62653                | -0.95586 | -0.68620               | 1.51134 | -1.28223 | 0.34421  |
| C3      | 0.97374                | 0.15469  | 0.05624                | 0.92411 | 0.08481  | 0.34802  |
| C4      | 1.39627                | 0.40961  | 1.48068                | 1.08023 | 0.83187  | 1.65475  |
| H1      | 2.60617                | -1.93616 | 0.91454                | 2.79946 | -1.15567 | -1.32886 |
| H2      | 2.82620                | -2.67034 | -0.75872               | 2.79081 | -2.75440 | -0.40769 |
| H3      | 1.43329                | -0.95550 | -1.75188               | 1.14670 | -1.91003 | 1.14748  |
| H4      | 1.18327                | -0.45956 | 2.09701                | 0.57522 | 1.79160  | 1.62484  |
| H5      | 2.46892                | 0.61345  | 1.50515                | 0.66947 | 0.23444  | 2.46499  |
| H6      | 0.86535                | 1.26549  | 1.88460                | 2.14507 | 0.99206  | 1.83936  |
| O1      | 1.19603                | 1.32725  | -0.78769               | 1.48731 | 0.80649  | -0.76877 |
| O2      | 0.80771                | 2.46346  | -0.25965               | 1.26733 | 2.10188  | -0.74872 |
| I1      | -1.24052               | -0.23524 | 0.00469                | -1.27818 | -0.14700 | -0.07948 |

|         | C$_2$H$_3$C(CH$_3$)OO-3 |         | C$_2$H$_3$C(CH$_3$)OO-4 |
|---------|------------------------|---------|------------------------|
| C1      | 2.42023                | -1.57657 | -0.79032               | -2.09404 | 2.05561 | -0.23337 |
| C2      | 1.68024                | -0.47482 | -0.81681               | -1.45288 | 0.98093 | -0.67437 |
| C3      | 0.93571                | 0.07554  | 0.34538                | -0.84861 | -0.07038 | 0.18443  |
| C4      | 1.23491                | -0.48570 | 1.71493                | -1.20903 | -0.08962 | 1.65103  |
| H1      | 2.53924                | -2.18424 | 0.09584                | -2.23902 | 2.25996 | 0.81805  |
| H2      | 2.93128                | -1.91350 | -1.68119               | -2.49535 | 2.77911 | -0.92876 |
| H3      | 1.58039                | 0.10246  | -1.72570               | -1.37242 | 0.81709 | -1.73759 |
| H4      | 0.97906                | -1.54059 | 1.75953                | -0.90779 | 0.83774 | 2.13170  |
| H5      | 2.29767                | -0.36570 | 1.93261                | -2.28846 | -0.21052 | 1.74812  |
| H6      | 0.65888                | 0.04133  | 2.47131                | -0.71205 | -0.91681 | 2.15140  |
| O1      | 1.16582                | 1.51383  | 0.48278                | -1.11908 | -1.40373 | -0.40570 |
| O2      | 1.05943                | 2.20140  | -0.62909               | -2.41620 | -1.63141 | -0.46285 |
| I1      | -1.25311               | -0.17155 | -0.08304               | 1.35622 | 0.02746 | -0.05285 |

|         | C$_2$H$_3$C(CH$_3$)OO-5 |         | C$_2$H$_3$C(CH$_3$)OO-6 |
|---------|------------------------|---------|------------------------|
| C1      | 2.63199                | -0.32753 | 1.34212                | -2.21329 | 1.86661 | -0.13279 |
| C2      | 1.58025                | 0.43451  | 1.07061                | -1.35573 | 1.19706 | 0.62693  |
| C3      | 0.84622                | 0.51248  | -0.22332               | -0.81042 | -0.15792 | 0.34280  |
| C4      | 0.84234                | 1.89870  | -0.84058               | -0.98690 | -1.15730 | 1.46646  |
| H1      | 3.05085                | -1.02375 | 0.63081                | -2.58662 | 1.47714 | -1.06850 |
| H2      | 3.10404                | -0.27200 | 2.31291                | -2.56987 | 2.83900 | 0.17570  |
| H3      | 1.19438                | 1.11423  | 1.82078                | -1.00151 | 1.62291 | 1.55827  |
| H4      | 0.25453                | 1.91526  | -1.75514               | -2.05006 | -1.29497 | 1.65900  |
| H5      | 0.42496                | 2.61708  | -0.13961               | -0.51121 | -0.77712 | 2.36771  |
| H6      | 1.87048                | 2.18744  | -1.06764               | -0.54090 | -2.11528 | 1.20931  |
| O1      | 1.40540                | -0.34583 | -1.24590               | -1.31447 | -0.67671 | -0.93398 |
| O2      | 1.35444                | -1.63359 | -0.98253               | -2.51365 | -1.21401 | -0.80801 |
|     | C\textsubscript{2}H\textsubscript{3}C(CH\textsubscript{3})IOO-7 | C\textsubscript{2}H\textsubscript{3}C(CH\textsubscript{3})IOO-8 |
|-----|-------------------------------------------------|-------------------------------------------------|
| I\textsubscript{1} | -1.27137 | -0.10966 | 0.14967 | 1.36006 | 0.05440 | -0.10917 |
| C\textsubscript{1} | -1.34558 | 2.21363 | -0.48362 | 0.93963 | -2.54732 | -0.33936 |
| C\textsubscript{2} | -1.75602 | 1.00984 | -0.12057 | 1.57755 | -1.40093 | -0.16830 |
| C\textsubscript{3} | -0.94824 | -0.12268 | 0.43106 | 1.01944 | -0.05363 | 0.17691 |
| C\textsubscript{4} | -1.09054 | -0.28983 | 1.93461 | 1.43250 | 0.42365 | 1.55613 |
| H\textsubscript{1} | -0.30037 | 2.48890 | -0.49447 | -0.13699 | -2.62340 | -0.28365 |
| H\textsubscript{2} | -2.06028 | 2.96254 | -0.79487 | 1.49325 | -3.45327 | -0.54332 |
| H\textsubscript{3} | -2.81580 | 0.77260 | -0.14826 | 2.66147 | -1.37674 | -0.24328 |
| H\textsubscript{4} | -0.58863 | -1.19407 | 2.27210 | 1.09754 | 1.44138 | 1.73165 |
| H\textsubscript{5} | -2.15054 | -0.35776 | 2.18794 | 2.52194 | 0.39079 | 1.63190 |
| H\textsubscript{6} | -0.66345 | 0.56922 | 2.44450 | 1.00866 | -0.23504 | 2.30973 |
| O\textsubscript{1} | -1.42679 | -1.39037 | -0.11580 | 1.57779 | 0.82542 | -0.86329 |
| O\textsubscript{2} | -1.66091 | -1.36151 | -1.40884 | 1.45852 | 2.10763 | -0.61295 |
| I\textsubscript{1} | 1.20987 | -0.00174 | -0.07243 | -1.18398 | 0.07286 | -0.00274 |

|     | C\textsubscript{2}H\textsubscript{3}C(CH\textsubscript{3})IOO-9 |
|-----|-------------------------------------------------|
| C\textsubscript{1} | -0.85679 | 2.49716 | -0.16648 |
| C\textsubscript{2} | -1.47631 | 1.33291 | -0.05901 |
| C\textsubscript{3} | -0.89363 | -0.01110 | 0.24765 |
| C\textsubscript{4} | -1.24917 | -0.52097 | 1.63195 |
| H\textsubscript{1} | 0.21643 | 2.59302 | -0.07871 |
| H\textsubscript{2} | -1.42190 | 3.40015 | -0.35148 |
| H\textsubscript{3} | -2.55621 | 1.28131 | -0.16151 |
| H\textsubscript{4} | -0.88415 | -1.53528 | 1.77847 |
| H\textsubscript{5} | -2.33304 | -0.51140 | 1.74686 |
| H\textsubscript{6} | -0.81049 | 0.13087 | 2.38376 |
| O\textsubscript{1} | -1.39059 | -0.97870 | -0.77997 |
| O\textsubscript{2} | -2.68859 | -1.16469 | -0.68266 |
| I\textsubscript{1} | 1.26940 | -0.15094 | -0.06681 |
Supplementary Table 4. Cartesian coordinates of optimized geometries of six conformers of iodoperoxy radical C(CH$_3$)$_2$ICHCH$_2$OO predicted with the B3LYP/aug-cc-pVTZ-pp method.

|        | $x$      | $y$      | $z$      |        | $x$      | $y$      | $z$      |
|--------|----------|----------|----------|--------|----------|----------|----------|
|        | (Z)-C(CH$_3$)$_2$ICHCH$_2$OO-1 |           |           |        | (Z)-C(CH$_3$)$_2$ICHCH$_2$OO-2 |           |           |
| C$_1$  | -1.93990 | -0.57964 | 0.47207  | 2.01366 | -0.00210 | 0.56055  |
| C$_2$  | -1.32212 | 0.75917  | 0.27465  | 4.01900 | -0.86918 | -0.17093 |
| C$_3$  | -0.04772 | 1.06450  | 0.06597  | -0.16532 | 1.19392  | 0.05182  |
| C$_4$  | 0.48084  | 2.45228  | -0.10650 | -0.96368 | 2.43584  | -0.18200 |
| H$_1$  | -1.25808 | -1.39637 | 0.25046  | 1.49103 | -0.95249 | 0.48647  |
| H$_2$  | -2.35891 | -0.69584 | 1.47152  | 2.51845 | 0.06865  | 1.52411  |
| H$_3$  | -2.02274 | 1.58870  | 0.31726  | 1.64187 | 2.13308  | 0.31147  |
| H$_4$  | 1.20142  | 2.69935  | 0.67429  | -1.45991 | 2.40194  | -1.15277 |
| H$_5$  | 0.99309  | 2.55786  | -1.06380 | -1.74173 | 2.55109  | 0.57383  |
| H$_6$  | -0.33814 | 3.17163  | -0.06623 | -0.31359 | 3.31121  | -0.15097 |
| O$_1$  | -3.05319 | -0.76906 | -0.46649 | 3.07480  | -0.00079 | -0.45979 |
| O$_2$  | -4.11955 | -0.09243 | -0.09691 | 4.01900  | -0.86918 | -0.17093 |
| I$_1$  | 1.47432  | -0.43795 | -0.02478 | -1.34028 | -0.59120 | -0.01699 |
|        | (Z)-C(CH$_3$)$_2$ICHCH$_2$OO-3 |           |           |        | (E)-C(CH$_3$)$_2$ICHCH$_2$OO-1 |           |           |
| C$_1$  | 1.98740  | -0.27280 | -0.85219 | -2.57328 | 0.03534  | 0.64762  |
| C$_2$  | 1.29033  | 0.97901  | -0.45186 | -1.14017 | -0.32932 | 0.45685  |
| C$_3$  | 0.02760  | 1.14266  | -0.07823 | -0.17255 | 0.52586  | 0.13698  |
| C$_4$  | -0.58880 | 2.45343  | 0.29199  | -0.26536 | 1.99478  | -0.11752 |
| H$_1$  | 1.41635  | -1.16882 | -0.62391 | -2.76358 | 1.10444  | 0.67260  |
| H$_2$  | 2.26209  | -0.26390 | -1.90828 | -2.99397 | -0.42833 | 1.53889  |
| H$_3$  | 1.90503  | 1.87504  | -0.48265 | -0.90496 | -1.37588 | 0.59529  |
| H$_4$  | -1.41382 | 2.70445  | -0.37598 | 0.34686  | 2.54988  | 0.59444  |
| H$_5$  | -0.99183 | 2.42042  | 1.30511  | 0.10817  | 2.23150  | -1.11436 |
| H$_6$  | 0.15797  | 3.24684  | 0.23845  | -1.29141 | 2.35219  | -0.04467 |
| O$_1$  | 3.28769  | -0.38556 | -0.18185 | -3.35388 | -0.50669 | -0.49474 |
| O$_2$  | 3.15351  | -0.65805 | 1.09953  | -4.63092 | -0.37782 | -0.30757 |
| I$_1$  | -1.34273 | -0.49583 | 0.01976  | 1.81399  | -0.23996 | -0.04844 |
|        | (E)-C(CH$_3$)$_2$ICHCH$_2$OO-2 |           |           |        | (E)-C(CH$_3$)$_2$ICHCH$_2$OO-3 |           |           |
| C$_1$  | 2.61026  | -0.25949 | -0.92265 | -2.63033 | 0.51860  | 0.50438  |
| C$_2$  | 1.17265  | -0.50923 | -0.60978 | -1.24380 | -0.02135 | 0.37574  |
| C$_3$  | 0.28715  | 0.43389  | -0.30052 | -0.16399 | 0.69476  | 0.07926  |
| C$_4$  | 0.48469  | 1.90915  | -0.18388 | -0.05107 | 2.15908  | -0.19607 |
| H$_1$  | 2.85268  | 0.78415  | -1.09531 | -2.70867 | 1.58317  | 0.30535  |
| H$_2$  | 2.94133  | -0.86217 | -1.76776 | -3.06718 | 0.28483  | 1.47452  |
| H$_3$  | 0.86578  | -1.54600 | -0.63521 | -1.16032 | -1.08614 | 0.54748  |
| H$_4$  | -0.15880 | 2.44249  | -0.88488 | 0.59284  | 2.64165  | 0.54054  |
| H$_5$  | 0.21981  | 2.24708  | 0.81854  | 0.39760  | 2.33045  | -1.17506 |
| H$_6$  | 1.51946  | 2.19086  | -0.36967 | -1.02312 | 2.65012  | -0.17494 |
| O$_1$  | 3.48715  | -0.72416 | 0.17047  | -3.51283 | -0.09460 | -0.50017 |
| O$_2$  | 3.47194  | 0.10625  | 1.18924  | -3.89364 | -1.30122 | -0.13977 |
| I$_1$  | -1.72154 | -0.18413 | 0.09731  | 1.71237  | -0.32725 | -0.01846 |
Supplementary Table 5. Comparison of experimental vibrational wavenumbers and IR intensities of (Z)-(CH₂I)HC=C(CH₃)I (1) with those of (Z)- and (E)-(CH₂I)HC=C(CH₃)I predicted with the B3LYP/aug-cc-pVTZ-pp method.

| Mode | This work (gas) | p-H₂  | (Z)-conformer | (E)-conformer |
|------|----------------|-------|---------------|---------------|
|      | ν/cm⁻¹   | Intensity       | ν/cm⁻¹ | Intensity | ν/cm⁻¹     | Intensity |
| v₁   | 3100     | 0.6             | 3109   | 1.1       |
| v₂   | 3010     | 8               | 2982.6 | 7         | 3035       | 6.7       | 3087     | 0.4       |
| v₃   | 2975     | 29              | 3031   | 2.1       | 3017       | 5.0       |
| v₄   | 2929     | 18              | 2972.4 | 18        | 3012       | 12.0      | 3023     | 12.1      |
| v₅   | 2888     | 4               | 2824.5 | 15        | 3000       | 5.9       | 3003     | 4.0       |
| v₆   | 2854     | 5               | 2847.9 | 5         | 2945       | 17.0      | 2953     | 9.4       |
| v₇   | 1641     | 17              | 1641.2 | 20        | 1644       | 33.5      | 1633     | 69.2      |
| v₈   | 1439.8   | 3               | 1453   | 3.5       | 1460       | 6.2       |
| v₉   | 1434     | 24              | 1432.0 | 29        | 1442       | 6.4       | 1440     | 4.6       |
| v₁₀  | 1430.3   | 18              | 1434   | 12.5      | 1435       | 11.2      |
| v₁₁  | 1384     | 3               | 1381.6 | 1         | 1383       | 2.1       | 1385     | 6.9       |
| v₁₂  | 1294     | 29              | 1299.1 | 41        | 1300       | 29.3      | 1339     | 2.2       |
| v₁₃  | 1169     |                | 1168.6 | 25        | 1157       | 30.8      | 1149     | 22.2      |
| v₁₄  | 1152     | 100             | 1153.0 | 100       | 1143       | 73.3      | 1134     | 120.9     |
| v₁₅  | 1095.0   | <1              | 1084   | 1.3       | 1059       | 3.8       |
| v₁₆  | 1063     | 24              | 1061.6 | 31        | 1049       | 31.9      | 1052     | 39.9      |
| v₁₇  | 1038.2   | <1              | 1043   | 1.2       | 1039       | 3.2       |
| v₁₈  | 965      | 2               | 965.3  | 1         | 957        | 2.7       | 917      | 4.7       |
| v₁₉  | 837      | 20              | 837.9  | 27        | 853        | 15.3      | 878      | 12.3      |
| v₂₀  | 810.6    | 8               | 806    | 8.6       | 825        | 1.2       |
| v₂₁  | 547.3    | 16              | 547    | 38.6      | 608        | 8.7       |
| v₂₂  | 530.3    | 10              | 519    | 11.4      | 509        | 24.3      |
| v₂₃  | 424      | 8.5             | 426    | 31.7      |
| v₂₄  | 410      | 9.9             | 353    | 11.5      |
| v₂₅  | 259      | 1.7             | 291    | 3.7       |
| v₂₆  | 264      | 3.0             | 257    | 1.2       |
| v₂₇  | 201      | 0.4             | 203    | 0.5       |

*aHaupa et al. J. Phys. Chem. A (submitted). bPercentage IR intensities relative to the most intense band near 1152 cm⁻¹. cHarmonic vibrational wavenumber x scaled according to y = (0.9708 ±0.0159) x + (9.3 ± 20.7); see text. dIn unit of km mol⁻¹. eoverlapped with the band at 1152 cm⁻¹.
Supplementary Table 6. Vibrational wavenumbers and IR intensities of (Z)- and (E)-C₂H₃CC(CH₃)I and (Z)- and (E)-(CH₂I)CHC(CH₃) predicted with the B3LYP/aug-cc-pVTZ-pp method.

| Mode | Symmetry | (Z)-C₂H₃CC(CH₃)I | (E)-C₂H₃CC(CH₃)I |
|------|----------|------------------|------------------|
|      |          | \( \nu / \text{cm}^{-1} \) | Intensity | \( \nu / \text{cm}^{-1} \) | Intensity |
| \( \nu_1 \) | a' | 3161 | 5.6 | 3158 | 6.8 |
| \( \nu_2 \) | a' | 3072 | 2.3 | 3076 | 2.8 |
| \( \nu_3 \) | a' | 3022 | 15.6 | 3072 | 4.9 |
| \( \nu_4 \) | a' | 3001 | 13.3 | 3019 | 10.4 |
| \( \nu_5 \) | a' | 2930 | 21.1 | 2939 | 14.1 |
| \( \nu_6 \) | a' | 1483 | 5.3 | 1487 | 0.6 |
| \( \nu_7 \) | a' | 1455 | 1.2 | 1453 | 0.1 |
| \( \nu_8 \) | a' | 1418 | 8.9 | 1410 | 23.4 |
| \( \nu_9 \) | a' | 1379 | 3.1 | 1374 | 7.5 |
| \( \nu_{10} \) | a' | 1261 | 37.0 | 1311 | 0.7 |
| \( \nu_{11} \) | a' | 1221 | 1.6 | 1214 | 5.6 |
| \( \nu_{12} \) | a' | 1108 | 35.3 | 1088 | 76.1 |
| \( \nu_{13} \) | a' | 1018 | 7.5 | 999 | 5.6 |
| \( \nu_{14} \) | a' | 887 | 10.3 | 888 | 8.3 |
| \( \nu_{15} \) | a' | 537 | 8.9 | 612 | 18.0 |
| \( \nu_{16} \) | a' | 438 | 6.2 | 347 | 2.4 |
| \( \nu_{17} \) | a' | 281 | 0.4 | 288 | 0.6 |
| \( \nu_{18} \) | a' | 194 | 0.1 | 225 | 0.2 |
| \( \nu_{19} \) | a'' | 2973 | 9.1 | 2979 | 8.7 |
| \( \nu_{20} \) | a'' | 1429 | 11.0 | 1431 | 10.5 |
| \( \nu_{21} \) | a'' | 1013 | 1.6 | 1016 | 1.5 |
| \( \nu_{22} \) | a'' | 930 | 10.4 | 951 | 9.5 |
| \( \nu_{23} \) | a'' | 803 | 40.8 | 790 | 44.0 |
| \( \nu_{24} \) | a'' | 560 | 2.5 | 555 | 2.0 |
| \( \nu_{25} \) | a'' | 314 | 5.5 | 313 | 3.5 |
| \( \nu_{26} \) | a'' | 219 | 0.4 | 175 | 0.2 |
| \( \nu_{27} \) | a'' | 148 | 0.5 | 91 | 0.2 |
| Mode | (Z)-(CH₂I)CHC(CH₃) | (E)-(CH₂I)CHC(CH₃) |
|------|---------------------|---------------------|
|      | 𝜈/cm⁻¹<sup>a</sup> | Intensity<sup>b</sup> | 𝜈/cm⁻¹<sup>a</sup> | Intensity<sup>b</sup> |
| v₁   | 3097                | 0.2                 | 3093                | 0.6                 |
| v₂   | 3027                | 4.2                 | 3026                | 2.8                 |
| v₃   | 2991                | 5.7                 | 3025                | 3.5                 |
| v₄   | 2968                | 11.4                | 2990                | 5.3                 |
| v₅   | 2945                | 12.1                | 2967                | 11.1                |
| v₆   | 2888                | 22.5                | 2889                | 16.8                |
| v₇   | 1704                | 30.4                | 1696                | 25.2                |
| v₈   | 1441                | 6.0                 | 1443                | 8.2                 |
| v₉   | 1435                | 9.0                 | 1430                | 9.0                 |
| v₁₀  | 1417                | 9.0                 | 1419                | 7.2                 |
| v₁₁  | 1365                | 2.1                 | 1365                | 4.9                 |
| v₁₂  | 1276                | 0.2                 | 1295                | 1.4                 |
| v₁₃  | 1146                | 72.2                | 1145                | 67.0                |
| v₁₄  | 1129                | 9.3                 | 1110                | 9.8                 |
| v₁₅  | 1064                | 6.6                 | 1031                | 0.1                 |
| v₁₆  | 1026                | 1.1                 | 1022                | 0.6                 |
| v₁₇  | 1012                | 1.3                 | 1007                | 4.5                 |
| v₁₈  | 902                 | 7.3                 | 884                 | 6.8                 |
| v₁₉  | 812                 | 5.7                 | 821                 | 11.6                |
| v₂₀  | 768                 | 19.7                | 779                 | 38.7                |
| v₂₁  | 509                 | 38.0                | 533                 | 41.2                |
| v₂₂  | 430                 | 1.8                 | 461                 | 0.2                 |
| v₂₃  | 250                 | 10.4                | 364                 | 15.9                |
| v₂₄  | 244                 | 3.1                 | 204                 | 0.4                 |
| v₂₅  | 203                 | 6.4                 | 191                 | 3.6                 |
| v₂₆  | 134                 | 1.9                 | 118                 | 0.0                 |
| v₂₇  | 80                  | 0.2                 | 62                  | 0.6                 |

<sup>a</sup>Harmonic vibrational wavenumber 𝜈 scaled according to 𝑦 = (0.9708 ± 0.0159) 𝜈 + (9.3 ± 20.7); see text.  
<sup>b</sup>In unit of km mol⁻¹.
Supplementary Table 7. Vibrational wavenumbers and IR intensities of four conformers of Criegee intermediates C$_2$H$_3$C(CH$_3$)OO and dioxole predicted with the B3LYP/aug-cc-pVTZ method.

| Mode | Symmetry | syn-trans-C$_2$H$_3$C(CH$_3$)OO Har | syn-trans-C$_2$H$_3$C(CH$_3$)OO Anharmonic | syn-cis-C$_2$H$_3$C(CH$_3$)OO Har | syn-cis-C$_2$H$_3$C(CH$_3$)OO Anharmonic |
|------|----------|-----------------|-----------------|-----------------|-----------------|
| $\nu_1$ | a' | 3155 | 3098 | 3.0 | 3159 | 3113 | 0.8 |
| $\nu_2$ | a' | 3086 | 3034 | 0.7 | 3090 | 3037 | 5.3 |
| $\nu_3$ | a' | 3076 | 3102 | 4.7 | 3072 | 3012 | 1.1 |
| $\nu_4$ | a' | 3070 | 2967 | 1.3 | 3058 | 3001 | 6.9 |
| $\nu_5$ | a' | 2954 | 2917 | 22.3 | 2946 | 2909 | 5.6 |
| $\nu_6$ | a' | 1626 | 1627 | 3.8 | 1630 | 1634 | 12.7 |
| $\nu_7$ | a' | 1455 | 1445 | 14.6 | 1460 | 1440 | 19.7 |
| $\nu_8$ | a' | 1454 | 1437 | 22.3 | 1452 | 1449 | 48.1 |
| $\nu_9$ | a' | 1425 | 1420 | 15.3 | 1403 | 1394 | 0.1 |
| $\nu_{10}$ | a' | 1367 | 1365 | 18.2 | 1366 | 1364 | 23.3 |
| $\nu_{11}$ | a' | 1304 | 1308 | 6.5 | 1308 | 1319 | 0.4 |
| $\nu_{12}$ | a' | 1278 | 1282 | 1.3 | 1244 | 1239 | 26.5 |
| $\nu_{13}$ | a' | 1045 | 1048 | 34.5 | 1084 | 1086 | 9.2 |
| $\nu_{14}$ | a' | 1000 | 1004 | 32.4 | 1011 | 1010 | 12.3 |
| $\nu_{15}$ | a' | 948 | 947 | 127.4 | 935 | 934 | 85.5 |
| $\nu_{16}$ | a' | 792 | 791 | 0.1 | 794 | 792 | 2.1 |
| $\nu_{17}$ | a' | 594 | 596 | 8.7 | 604 | 604 | 29.1 |
| $\nu_{18}$ | a' | 490 | 489 | 8.5 | 479 | 478 | 5.8 |
| $\nu_{19}$ | a' | 331 | 333 | 5.1 | 325 | 313 | 6.7 |
| $\nu_{20}$ | a' | 259 | 254 | 8.1 | 232 | 221 | 5.9 |
| $\nu_{21}$ | a'' | 2990 | 2923 | 0.6 | 2982 | 2914 | 0.8 |
| $\nu_{22}$ | a'' | 1409 | 1396 | 8.9 | 1408 | 1393 | 9.8 |
| $\nu_{23}$ | a'' | 1020 | 1033 | 0.1 | 1019 | 1017 | 8.9 |
| $\nu_{24}$ | a'' | 1004 | 951 | 16.9 | 999 | 947 | 12.4 |
| $\nu_{25}$ | a'' | 948 | 939 | 43.6 | 971 | 968 | 33.9 |
| $\nu_{26}$ | a'' | 676 | 666 | 5.6 | 659 | 647 | 7.7 |
| $\nu_{27}$ | a'' | 459 | 448 | 1.1 | 445 | 435 | 1.2 |
| $\nu_{28}$ | a'' | 284 | 267 | 0.2 | 271 | 272 | 1.4 |
| Mode | Symmetry | \( v_{29} \) | \( a'' \) | \( v_{30} \) | \( a'' \) | \( \text{anti-trans-C}_2\text{H}_3\text{C(CH}_3\text{)}\text{OO} \) | \( \text{anti-cis-C}_2\text{H}_3\text{C(CH}_3\text{)}\text{OO} \) |
|------|----------|-------------|-------------|-------------|-------------|------------------|------------------|
|      |          | Harmonic\(^a\) | Anharmonic | Intensity\(^b\) | Harmonic\(^a\) | Anharmonic | Intensity\(^b\) |
| \( v_1 \) | \( a' \) | 3161 | 3120 | 2.3 | 3196 | 3128 | 1.9 |
| \( v_2 \) | \( a' \) | 3129 | 3074 | 8.8 | 3071 | 3017 | 13.2 |
| \( v_3 \) | \( a' \) | 3075 | 2988 | 1.7 | 3059 | 3092 | 4.8 |
| \( v_4 \) | \( a' \) | 3063 | 3001 | 2.3 | 3057 | 2922 | 6.6 |
| \( v_5 \) | \( a' \) | 2968 | 2945 | 7.8 | 2951 | 2910 | 4.7 |
| \( v_6 \) | \( a' \) | 1612 | 1617 | 4.7 | 1602 | 1594 | 28.5 |
| \( v_7 \) | \( a' \) | 1469 | 1465 | 1.3 | 1480 | 1471 | 12.5 |
| \( v_8 \) | \( a' \) | 1425 | 1427 | 38.5 | 1423 | 1432 | 50.9 |
| \( v_9 \) | \( a' \) | 1391 | 1385 | 20.9 | 1419 | 1419 | 21.3 |
| \( v_{10} \) | \( a' \) | 1369 | 1360 | 3.6 | 1379 | 1373 | 3.0 |
| \( v_{11} \) | \( a' \) | 1338 | 1333 | 15.9 | 1309 | 1313 | 6.4 |
| \( v_{12} \) | \( a' \) | 1250 | 1246 | 0.5 | 1231 | 1229 | 22.7 |
| \( v_{13} \) | \( a' \) | 1050 | 1055 | 124.6 | 1081 | 1093 | 4.2 |
| \( v_{14} \) | \( a' \) | 999 | 1001 | 82.4 | 1014 | 1016 | 52.2 |
| \( v_{15} \) | \( a' \) | 957 | 954 | 38.3 | 942 | 938 | 59.8 |
| \( v_{16} \) | \( a' \) | 780 | 789 | 4.4 | 802 | 814 | 4.9 |
| \( v_{17} \) | \( a' \) | 625 | 624 | 6.6 | 622 | 625 | 4.6 |
| \( v_{18} \) | \( a' \) | 475 | 474 | 2.5 | 407 | 404 | 7.0 |
| \( v_{19} \) | \( a' \) | 323 | 331 | 3.2 | 340 | 338 | 2.8 |
| \( v_{20} \) | \( a' \) | 247 | 256 | 4.8 | 302 | 293 | 8.6 |
| \( v_{21} \) | \( a'' \) | 3017 | 2960 | 5.1 | 2996 | 2925 | 5.3 |
| \( v_{22} \) | \( a'' \) | 1439 | 1433 | 10.7 | 1441 | 1437 | 8.9 |
| \( v_{23} \) | \( a'' \) | 1029 | 1031 | 12.2 | 1028 | 1015 | 2.2 |
| \( v_{24} \) | \( a'' \) | 1025 | 1006 | 4.9 | 1010 | 991 | 7.1 |
| \( v_{25} \) | \( a'' \) | 962 | 960 | 38.4 | 999 | 1058 | 39.8 |
| \( v_{26} \) | \( a'' \) | 712 | 707 | 4.4 | 710 | 705 | 5.5 |
| \( v_{27} \) | \( a'' \) | 385 | 383 | 1.0 | 385 | 368 | 0.2 |
| \( v_{28} \) | \( a'' \) | 265 | 258 | 0.1 | 280 | 271 | 0.4 |
| \( v_{29} \) | \( a'' \) | 120 | 111 | 1.2 | 169 | 223 | 1.7 |
| \( v_{30} \) | \( a'' \) | 91 | 125 | 0.1 | 122 | 51 | 0.1 |
| Mode | Symmetry | Harmonic<sup>a</sup> | Anharmonic | Intensity<sup>b</sup> |
|------|----------|----------------------|-------------|----------------------|
| v₁   | a        | 3171                 | 3128        | 0.6                  |
| v₂   | a        | 3052                 | 2989        | 8.0                  |
| v₃   | a        | 3011                 | 2946        | 7.1                  |
| v₄   | a        | 2963                 | 2938        | 16.9                 |
| v₅   | a        | 2927                 | 2701        | 37.8                 |
| v₆   | a        | 2895                 | 2894        | 78.5                 |
| v₇   | a        | 1700                 | 1696        | 56.9                 |
| v₈   | a        | 1500                 | 1495        | 3.4                  |
| v₉   | a        | 1462                 | 1449        | 8.2                  |
| v₁₀  | a        | 1446                 | 1434        | 7.7                  |
| v₁₁  | a        | 1392                 | 1379        | 3.8                  |
| v₁₂  | a        | 1341                 | 1335        | 4.4                  |
| v₁₃  | a        | 1266                 | 1268        | 40.8                 |
| v₁₄  | a        | 1188                 | 1178        | 20.0                 |
| v₁₅  | a        | 1153                 | 1115        | 0.2                  |
| v₁₆  | a        | 1056                 | 1045        | 0.7                  |
| v₁₇  | a        | 1038                 | 1026        | 5.9                  |
| v₁₈  | a        | 1017                 | 1028        | 9.8                  |
| v₁₉  | a        | 1011                 | 1001        | 1.1                  |
| v₂₀  | a        | 953                  | 952         | 31.2                 |
| v₂₁  | a        | 906                  | 877         | 6.7                  |
| v₂₂  | a        | 839                  | 829         | 13.4                 |
| v₂₃  | a        | 756                  | 760         | 3.2                  |
| v₂₄  | a        | 708                  | 697         | 31.0                 |
| v₂₅  | a        | 622                  | 611         | 2.7                  |
| v₂₆  | a        | 564                  | 554         | 0.0                  |
| v₂₇  | a        | 339                  | 331         | 2.2                  |
| v₂₈  | a        | 237                  | 262         | 5.1                  |
| v₂₉  | a        | 173                  | 112         | 1.0                  |
| v₃₀  | a        | 60                   | -888        | 2.1                  |

<sup>a</sup>Harmonic vibrational wavenumber x scaled according to y = (0.9708 ± 0.0159) x + (9.3 ± 20.7); see text. <sup>b</sup>In unit of km mol⁻¹.
Supplementary Table 8. Vibrational wavenumbers and IR intensities of nine conformers of iodoperoxy radical C$_2$H$_3$C(CH$_3$)IOO predicted with the B3LYP/aug-cc-pVTZ-pp method.

| Mode | C$_2$H$_3$C(CH$_3$)IOO-1 | C$_2$H$_3$C(CH$_3$)IOO-2 | C$_2$H$_3$C(CH$_3$)IOO-3 |
|------|--------------------------|--------------------------|--------------------------|
|      | v cm$^{-1}$ | Int.$^b$ | v cm$^{-1}$ | Int.$^b$ | v cm$^{-1}$ | Int.$^b$ |
| v$_1$ | 3148 | 3.7 | 3157 | 1.8 | 3146 | 3.5 |
| v$_2$ | 3083 | 0.3 | 3084 | 1.0 | 3102 | 1.5 |
| v$_3$ | 3073 | 0.5 | 3073 | 0.1 | 3068 | 3.0 |
| v$_4$ | 3069 | 2.2 | 3071 | 3.1 | 3062 | 1.8 |
| v$_5$ | 3041 | 4.5 | 3034 | 4.4 | 3037 | 4.2 |
| v$_6$ | 2961 | 9.8 | 2956 | 9.1 | 2964 | 8.9 |
| v$_7$ | 1654 | 1.0 | 1647 | 1.2 | 1649 | 1.1 |
| v$_8$ | 1457 | 4.3 | 1455 | 4.9 | 1456 | 2.2 |
| v$_9$ | 1452 | 2.7 | 1442 | 2.1 | 1454 | 5.5 |
| v$_{10}$ | 1421 | 15.7 | 1422 | 13.2 | 1420 | 15.8 |
| v$_{11}$ | 1376 | 15.4 | 1376 | 13.6 | 1383 | 12.2 |
| v$_{12}$ | 1305 | 0.1 | 1304 | 0.1 | 1299 | 0.7 |
| v$_{13}$ | 1247 | 9.3 | 1205 | 14.3 | 1245 | 11.2 |
| v$_{14}$ | 1145 | 4.2 | 1170 | 14.0 | 1155 | 6.4 |
| v$_{15}$ | 1108 | 31.7 | 1103 | 10.2 | 1102 | 28.2 |
| v$_{16}$ | 1054 | 56.8 | 1050 | 74.7 | 1054 | 50.9 |
| v$_{17}$ | 1008 | 13.4 | 1020 | 10.0 | 1017 | 14.1 |
| v$_{18}$ | 985 | 3.6 | 1002 | 8.2 | 985 | 4.1 |
| v$_{19}$ | 954 | 39.3 | 956 | 37.3 | 953 | 38.6 |
| v$_{20}$ | 847 | 11.4 | 870 | 7.3 | 851 | 11.0 |
| v$_{21}$ | 767 | 69.8 | 754 | 61.0 | 735 | 75.2 |
| v$_{22}$ | 680 | 12.0 | 686 | 26.3 | 701 | 6.1 |
| v$_{23}$ | 569 | 4.7 | 569 | 6.8 | 594 | 9.7 |
| v$_{24}$ | 484 | 27.8 | 522 | 19.6 | 462 | 20.1 |
| v$_{25}$ | 416 | 8.3 | 413 | 10.9 | 423 | 8.2 |
| v$_{26}$ | 332 | 2.5 | 329 | 4.0 | 332 | 0.8 |
| v$_{27}$ | 286 | 0.6 | 268 | 0.3 | 268 | 2.3 |
| v$_{28}$ | 261 | 0.5 | 259 | 0.4 | 258 | 0.8 |
| v$_{29}$ | 249 | 4.9 | 243 | 6.9 | 246 | 6.4 |
| v$_{30}$ | 219 | 4.5 | 222 | 2.7 | 230 | 1.8 |
| v$_{31}$ | 213 | 1.0 | 207 | 0.3 | 215 | 1.8 |
| v$_{32}$ | 102 | 0.1 | 95 | 0.4 | 104 | 0.2 |
| v$_{33}$ | 89 | 0.2 | 70 | 0.1 | 96 | 0.1 |
| Mode | \(\nu^a/\text{cm}^{-1}\) | Int. \(b\) | \(\nu^a/\text{cm}^{-1}\) | Int. \(b\) | \(\nu^a/\text{cm}^{-1}\) | Int. \(b\) |
|------|------------------|--------|------------------|--------|------------------|--------|
| \(v_1\) | 3148 | 3.9 | 3154 | 2.0 | 3155 | 1.7 |
| \(v_2\) | 3083 | 0.2 | 3079 | 0.9 | 3079 | 1.5 |
| \(v_3\) | 3069 | 2.9 | 3069 | 1.9 | 3069 | 2.1 |
| \(v_4\) | 3057 | 3.0 | 3058 | 3.3 | 3053 | 4.0 |
| \(v_5\) | 3039 | 2.7 | 3032 | 4.6 | 3041 | 2.2 |
| \(v_6\) | 2969 | 4.0 | 2960 | 9.1 | 2973 | 3.4 |
| \(v_7\) | 1652 | 1.0 | 1648 | 0.9 | 1648 | 0.4 |
| \(v_8\) | 1455 | 2.6 | 1453 | 6.1 | 1455 | 6.7 |
| \(v_9\) | 1455 | 4.7 | 1447 | 2.8 | 1447 | 1.8 |
| \(v_{10}\) | 1419 | 16.0 | 1423 | 14.4 | 1421 | 14.2 |
| \(v_{11}\) | 1375 | 11.1 | 1381 | 10.9 | 1375 | 13.2 |
| \(v_{12}\) | 1306 | 0.3 | 1303 | 0.1 | 1301 | 0.0 |
| \(v_{13}\) | 1212 | 9.4 | 1199 | 14.5 | 1183 | 10.8 |
| \(v_{14}\) | 1131 | 15.5 | 1137 | 10.5 | 1129 | 8.7 |
| \(v_{15}\) | 1098 | 20.5 | 1104 | 13.9 | 1085 | 8.9 |
| \(v_{16}\) | 1059 | 83.9 | 1061 | 79.9 | 1067 | 107.5 |
| \(v_{17}\) | 1005 | 11.2 | 1019 | 7.8 | 1015 | 3.8 |
| \(v_{18}\) | 983 | 4.5 | 995 | 6.8 | 999 | 9.4 |
| \(v_{19}\) | 952 | 38.0 | 953 | 38.7 | 956 | 33.8 |
| \(v_{20}\) | 881 | 17.9 | 872 | 7.6 | 885 | 9.6 |
| \(v_{21}\) | 740 | 74.8 | 754 | 58.4 | 715 | 66.8 |
| \(v_{22}\) | 712 | 1.4 | 681 | 22.4 | 711 | 17.0 |
| \(v_{23}\) | 538 | 9.3 | 615 | 21.1 | 626 | 10.6 |
| \(v_{24}\) | 522 | 9.0 | 514 | 6.9 | 491 | 3.3 |
| \(v_{25}\) | 394 | 3.1 | 365 | 10.0 | 378 | 3.6 |
| \(v_{26}\) | 324 | 4.4 | 357 | 1.2 | 341 | 3.5 |
| \(v_{27}\) | 288 | 1.9 | 268 | 0.9 | 280 | 0.7 |
| \(v_{28}\) | 259 | 1.4 | 251 | 2.3 | 253 | 1.5 |
| \(v_{29}\) | 249 | 2.7 | 246 | 3.8 | 247 | 3.8 |
| \(v_{30}\) | 223 | 2.3 | 235 | 0.9 | 222 | 2.2 |
| \(v_{31}\) | 181 | 2.2 | 194 | 1.1 | 192 | 0.8 |
| \(v_{32}\) | 98 | 0.2 | 132 | 0.1 | 106 | 0.2 |
| \(v_{33}\) | 85 | 0.5 | 101 | 0.4 | 76 | 0.9 |
| Mode | C₂H₃C(CH₃)IOO-7 | Int. | C₂H₃C(CH₃)IOO-8 | Int. | C₂H₃C(CH₃)IOO-9 | Int. |
|------|----------------|------|----------------|------|----------------|------|
|      | ν a/cm⁻¹       |      | ν a/cm⁻¹       |      | ν a/cm⁻¹       |      |
| v₁   | 3147           | 0.4  | 3148           | 3.2  | 3145           | 3.7  |
| v₂   | 3067           | 1.8  | 3069           | 0.4  | 3065           | 1.9  |
| v₃   | 3061           | 3.1  | 3067           | 3.2  | 3053           | 4.1  |
| v₄   | 3045           | 3.3  | 3040           | 6.1  | 3051           | 0.3  |
| v₅   | 3029           | 5.9  | 3035           | 3.3  | 3036           | 3.8  |
| v₆   | 2958           | 11.0 | 2956           | 12.5 | 2968           | 4.3  |
| v₇   | 1669           | 6.9  | 1670           | 6.2  | 1665           | 7.9  |
| v₈   | 1452           | 4.7  | 1456           | 3.4  | 1455           | 4.5  |
| v₉   | 1447           | 1.8  | 1443           | 1.6  | 1445           | 2.1  |
| v₁₀  | 1416           | 21.2 | 1417           | 21.9 | 1416           | 17.5 |
| v₁₁  | 1380           | 9.8  | 1373           | 13.0 | 1373           | 10.7 |
| v₁₂  | 1301           | 4.0  | 1302           | 4.9  | 1292           | 5.0  |
| v₁₃  | 1192           | 21.5 | 1192           | 37.1 | 1167           | 53.8 |
| v₁₄  | 1146           | 15.4 | 1143           | 3.0  | 1129           | 4.7  |
| v₁₅  | 1082           | 44.8 | 1085           | 46.6 | 1090           | 56.2 |
| v₁₆  | 1060           | 30.8 | 1051           | 22.6 | 1040           | 14.7 |
| v₁₇  | 1024           | 6.6  | 1023           | 10.1 | 1019           | 8.1  |
| v₁₈  | 987            | 3.4  | 993            | 4.7  | 999            | 6.2  |
| v₁₉  | 962            | 36.9 | 970            | 38.5 | 963            | 36.0 |
| v₂₀  | 862            | 11.7 | 854            | 13.2 | 876            | 11.5 |
| v₂₁  | 749            | 42.2 | 756            | 33.7 | 725            | 27.3 |
| v₂₂  | 689            | 13.0 | 657            | 13.4 | 676            | 5.4  |
| v₂₃  | 568            | 14.9 | 595            | 11.9 | 632            | 21.3 |
| v₂₄  | 501            | 4.1  | 485            | 12.1 | 435            | 6.5  |
| v₂₅  | 419            | 14.9 | 397            | 11.7 | 377            | 2.8  |
| v₂₆  | 323            | 1.2  | 327            | 4.1  | 361            | 1.0  |
| v₂₇  | 285            | 3.5  | 316            | 0.4  | 307            | 4.4  |
| v₂₈  | 256            | 1.7  | 265            | 0.1  | 264            | 1.2  |
| v₂₉  | 255            | 1.5  | 260            | 2.2  | 251            | 0.1  |
| v₃₀  | 232            | 0.5  | 220            | 0.7  | 193            | 1.1  |
| v₃₁  | 177            | 0.6  | 186            | 0.4  | 187            | 0.4  |
| v₃₂  | 91             | 0.4  | 88             | 0.3  | 110            | 0.8  |
| v₃₃  | 72             | 0.4  | 66             | 0.3  | 80             | 0.3  |

*a*Harmonic vibrational wavenumber ν scaled according to ν = (0.9708 ± 0.0159)x + (9.3 ± 20.7); see text. *b*In unit of km mol⁻¹.
Supplementary Table 9. Vibrational wavenumbers and IR intensities of six conformers of iodoperoxy radical C(CH$_3$)ICHCH$_2$OO predicted with the B3LYP/aug-cc-pVTZ-pp method.

| Mode | (Z)-C(CH$_3$)ICHCH$_2$OO-1 | (Z)-C(CH$_3$)ICHCH$_2$OO-2 | (Z)-C(CH$_3$)ICHCH$_2$OO-3 |
|------|-----------------------------|-----------------------------|-----------------------------|
|      | $\nu$ a/cm$^{-1}$ | Int. b | $\nu$ a/cm$^{-1}$ | Int. b | $\nu$ a/cm$^{-1}$ | Int. b |
| v1   | 3054 | 2.0 | 3045 | 6.5 | 3046 | 4.5 |
| v2   | 3040 | 1.4 | 3032 | 1.7 | 3033 | 2.5 |
| v3   | 3015 | 12.1 | 3016 | 11.3 | 3015 | 11.7 |
| v4   | 3005 | 5.0 | 3006 | 4.6 | 3005 | 5.0 |
| v5   | 2980 | 8.6 | 2978 | 6.5 | 2973 | 11.5 |
| v6   | 2948 | 13.0 | 2948 | 12.8 | 2948 | 13.8 |
| v7   | 1668 | 24.7 | 1668 | 32.9 | 1669 | 23.6 |
| v8   | 1453 | 4.1 | 1453 | 4.6 | 1453 | 4.4 |
| v9   | 1439 | 4.8 | 1450 | 6.1 | 1439 | 5.4 |
| v10  | 1435 | 12.9 | 1434 | 12.8 | 1435 | 12.4 |
| v11  | 1384 | 3.0 | 1384 | 3.5 | 1384 | 3.0 |
| v12  | 1337 | 4.6 | 1343 | 18.5 | 1338 | 7.4 |
| v13  | 1272 | 44.4 | 1282 | 42.3 | 1280 | 40.8 |
| v14  | 1239 | 7.0 | 1196 | 10.9 | 1234 | 9.4 |
| v15  | 1137 | 38.1 | 1154 | 9.2 | 1127 | 21.4 |
| v16  | 1113 | 23.7 | 1114 | 39.8 | 1106 | 34.0 |
| v17  | 1057 | 8.5 | 1065 | 17.9 | 1061 | 7.6 |
| v18  | 1045 | 0.9 | 1045 | 0.6 | 1045 | 0.6 |
| v19  | 1015 | 11.4 | 1003 | 3.6 | 1012 | 6.0 |
| v20  | 936 | 23.8 | 951 | 22.8 | 948 | 13.5 |
| v21  | 837 | 21.6 | 862 | 16.0 | 860 | 35.9 |
| v22  | 820 | 13.7 | 811 | 9.7 | 796 | 8.5 |
| v23  | 563 | 2.3 | 582 | 35.5 | 566 | 6.6 |
| v24  | 517 | 18.7 | 462 | 2.8 | 506 | 12.6 |
| v25  | 428 | 6.9 | 427 | 8.8 | 432 | 10.5 |
| v26  | 421 | 3.2 | 407 | 1.2 | 419 | 3.6 |
| v27  | 347 | 3.9 | 344 | 4.9 | 330 | 5.1 |
| v28  | 276 | 0.7 | 275 | 1.1 | 275 | 1.0 |
| v29  | 214 | 0.4 | 209 | 0.4 | 217 | 1.0 |
| v30  | 164 | 2.3 | 184 | 1.6 | 185 | 1.4 |
| v31  | 144 | 0.4 | 122 | 1.4 | 145 | 1.6 |
| v32  | 82 | 3.2 | 66 | 0.1 | 75 | 0.9 |
| v33  | 44 | 3.2 | 41 | 2.4 | 34 | 2.1 |
| Mode | (E)-C(CH₃)ICHCH₂OO-1 | (E)-C(CH₃)ICHCH₂OO-2 | (E)-C(CH₃)ICHCH₂OO-3 |
|------|----------------------|---------------------|---------------------|
| v₁   | 3093 cm⁻¹ 0.6         | 3093 cm⁻¹ 0.9       | 3094 cm⁻¹ 0.4       |
| v₂   | 3049 cm⁻¹ 10.2        | 3059 cm⁻¹ 7.1       | 3058 cm⁻¹ 8.7       |
| v₃   | 3027 cm⁻¹ 12.8        | 3032 cm⁻¹ 12.0      | 3024 cm⁻¹ 15.5      |
| v₄   | 3008 cm⁻¹ 3.3         | 3008 cm⁻¹ 3.6       | 3007 cm⁻¹ 3.8       |
| v₅   | 2988 cm⁻¹ 9.0         | 2992 cm⁻¹ 17.0      | 2988 cm⁻¹ 13.2      |
| v₆   | 2957 cm⁻¹ 7.2         | 2958 cm⁻¹ 7.0       | 2956 cm⁻¹ 8.9       |
| v₇   | 1652 cm⁻¹ 60.3        | 1650 cm⁻¹ 52.1      | 1654 cm⁻¹ 43.9      |
| v₈   | 1464 cm⁻¹ 6.1         | 1459 cm⁻¹ 7.9       | 1456 cm⁻¹ 7.7       |
| v₉   | 1443 cm⁻¹ 4.4         | 1438 cm⁻¹ 4.2       | 1438 cm⁻¹ 10.4      |
| v₁₀  | 1436 cm⁻¹ 11.7        | 1434 cm⁻¹ 10.5      | 1435 cm⁻¹ 2.8       |
| v₁₁  | 1385 cm⁻¹ 6.4         | 1386 cm⁻¹ 6.1       | 1386 cm⁻¹ 6.5       |
| v₁₂  | 1351 cm⁻¹ 27.4        | 1346 cm⁻¹ 10.5      | 1345 cm⁻¹ 9.0       |
| v₁₃  | 1314 cm⁻¹ 26.3        | 1312 cm⁻¹ 14.4      | 1303 cm⁻¹ 8.6       |
| v₁₄  | 1195 cm⁻¹ 26.4        | 1239 cm⁻¹ 15.3      | 1244 cm⁻¹ 22.8      |
| v₁₅  | 1149 cm⁻¹ 8.9         | 1126 cm⁻¹ 25.2      | 1136 cm⁻¹ 29.4      |
| v₁₆  | 1102 cm⁻¹ 70.7        | 1106 cm⁻¹ 59.9      | 1102 cm⁻¹ 60.5      |
| v₁₇  | 1061 cm⁻¹ 14.6        | 1053 cm⁻¹ 4.2       | 1053 cm⁻¹ 7.5       |
| v₁₈  | 1042 cm⁻¹ 0.6         | 1042 cm⁻¹ 0.6       | 1041 cm⁻¹ 0.7       |
| v₁₉  | 966 cm⁻¹ 5.1          | 984 cm⁻¹ 12.4       | 981 cm⁻¹ 8.5        |
| v₂₀  | 931 cm⁻¹ 17.4         | 910 cm⁻¹ 7.5        | 917 cm⁻¹ 9.2        |
| v₂₁  | 875 cm⁻¹ 17.8         | 872 cm⁻¹ 26.0       | 856 cm⁻¹ 14.8       |
| v₂₂  | 829 cm⁻¹ 6.1          | 794 cm⁻¹ 15.7       | 825 cm⁻¹ 17.2       |
| v₂₃  | 610 cm⁻¹ 10.6         | 612 cm⁻¹ 16.9       | 609 cm⁻¹ 19.9       |
| v₂₄  | 515 cm⁻¹ 35.1         | 544 cm⁻¹ 2.8        | 541 cm⁻¹ 0.6        |
| v₂₅  | 447 cm⁻¹ 1.8          | 442 cm⁻¹ 11.9       | 440 cm⁻¹ 9.5        |
| v₂₆  | 350 cm⁻¹ 5.0          | 371 cm⁻¹ 10.6       | 391 cm⁻¹ 7.7        |
| v₂₇  | 305 cm⁻¹ 0.6          | 318 cm⁻¹ 1.7        | 290 cm⁻¹ 1.6        |
| v₂₈  | 279 cm⁻¹ 2.0          | 286 cm⁻¹ 2.2        | 274 cm⁻¹ 1.6        |
| v₂₉  | 211 cm⁻¹ 0.2          | 213 cm⁻¹ 0.1        | 215 cm⁻¹ 0.9        |
| v₃₀  | 180 cm⁻¹ 0.3          | 179 cm⁻¹ 0.2        | 182 cm⁻¹ 0.2        |
| v₃₁  | 90 cm⁻¹ 1.9           | 130 cm⁻¹ 0.4        | 121 cm⁻¹ 0.4        |
| v₃₂  | 70 cm⁻¹ 0.0           | 64 cm⁻¹ 1.7         | 67 cm⁻¹ 2.5         |
| v₃₃  | 43 cm⁻¹ 3.1           | 50 cm⁻¹ 2.6         | 53 cm⁻¹ 1.7         |

*aHarmonic vibrational wavenumber x scaled according to \( y = (0.9708 \pm 0.0159) x + (9.3 \pm 20.7) \); see text. *bIn unit of km mol⁻¹.
Supplementary Table 10. Rotational parameters and ratios of types for each vibrational state of four conformers of Criegee intermediates MKVO predicted with the B3LYP/aug-cc-pVTZ method.

| $v_i$ | Sym. | syn-trans-C$_2$H$_3$C(CH$_3$)OO | syn-cis-C$_2$H$_3$C(CH$_3$)OO |
|-------|------|-------------------------------|-------------------------------|
|       |      | $A''/A''$ | $B'/B''$ | $C'/C''$ | type ratio | $A''/A''$ | $B'/B''$ | $C'/C''$ | type ratio |
| $v_1$ | a'   | 0.99950 0.99946 0.99950 | $a/b = 7/93$ | 0.99986 0.99933 0.99952 | $a/b = 86/14$ |
| $v_2$ | a'   | 0.99930 0.99940 0.99939 | $a/b = 98/2$ | 0.99980 0.99894 0.99922 | $a/b = 25/75$ |
| $v_3$ | a'   | 0.99913 0.99952 0.99944 | $a/b = 11/89$ | 0.99990 0.99938 0.99952 | $a/b = 18/82$ |
| $v_4$ | a'   | 0.99909 0.99966 0.99957 | $a/b = 37/63$ | 0.99945 0.99999 0.99991 | $a/b = 1/99$ |
| $v_5$ | a'   | 0.99998 0.99969 0.99989 | $a/b = 4/96$ | 1.00016 0.99981 1.00006 | $a/b = 65/35$ |
| $v_6$ | a'   | 1.00016 0.99822 0.99848 | $a/b = 71/29$ | 0.99852 0.99918 0.99890 | $a/b = 64/36$ |
| $v_7$ | a'   | 0.99972 0.99964 0.99960 | $a/b = 2/98$ | 0.99859 0.99936 0.99917 | $a/b = 96/4$ |
| $v_8$ | a'   | 0.99797 0.99857 0.99893 | $a/b = 99/1$ | 0.99994 0.99737 0.99948 | $a/b = 33/67$ |
| $v_9$ | a'   | 1.00039 0.99924 0.99917 | $a/b = 27/73$ | 0.99938 0.99960 1.00011 | $a/b = 66/4$ |
| $v_{10}$ | a'   | 0.99128 0.99982 0.99923 | $a/b = 1/99$ | 0.99483 0.99936 0.99868 | $a/b = 76/24$ |
| $v_{11}$ | a'   | 0.99955 0.99859 0.99817 | $a/b = 41/59$ | 0.99966 1.00025 0.99965 | $a/b = 60/40$ |
| $v_{12}$ | a'   | 0.99972 1.00023 0.99891 | $a/b = 97/3$ | 0.99930 0.99850 0.99765 | $a/b = 52/48$ |
| $v_{13}$ | a'   | 1.00153 1.00087 0.99958 | $a/b = 89/11$ | 1.00174 0.99998 0.99911 | $a/b = 31/69$ |
| $v_{14}$ | a'   | 0.99851 0.99864 0.99925 | $a/b = 88/12$ | 0.99933 0.99777 0.99945 | $a/b = 93/7$ |
| $v_{15}$ | a'   | 1.00075 0.99795 0.99812 | $a/b = 95/5$ | 1.00008 0.99698 0.99807 | $a/b = 63/37$ |
| $v_{16}$ | a'   | 0.99779 0.99940 0.99862 | $a/b = 99/1$ | 0.99912 0.99895 0.99844 | $a/b = 84/16$ |
| $v_{17}$ | a'   | 1.00076 0.99943 0.99926 | $a/b = 99/1$ | 0.99857 0.99926 0.99910 | $a/b = 90/10$ |
| $v_{18}$ | a'   | 1.00058 0.99957 0.99963 | $a/b = 43/5$ | 1.00187 0.99984 0.99954 | $a/b = 99/1$ |
| $v_{19}$ | a'   | 0.99927 0.99987 0.99865 | $a/b = 42/58$ | 0.99755 1.00223 0.99952 | $a/b = 1/99$ |
| $v_{20}$ | a'   | 1.00039 0.99918 0.99869 | $a/b = 90/10$ | 0.99860 0.99969 0.99842 | $a/b = 74/26$ |
| $v_{21}$ | a''  | 0.99909 0.99966 0.99957 | $c$ | 1.00091 0.99973 1.00014 | $c$ |
| $v_{22}$ | a''  | 1.00878 0.99964 1.00024 | $c$ | 1.00587 0.99975 1.00026 | $c$ |
| $v_{23}$ | a''  | 1.00070 1.00069 0.99997 | $c$ | 0.99898 0.99953 0.99997 | $c$ |
| $v_{24}$ | a''  | 0.99883 0.99864 1.00018 | $c$ | 0.99865 0.99981 1.00029 | $c$ |
| $v_{25}$ | a''  | 0.99682 0.99944 1.00018 | $c$ | 0.99891 0.99928 1.00002 | $c$ |
| $v_{26}$ | a''  | 1.00063 0.99996 1.00022 | $c$ | 1.00070 1.00002 1.00041 | $c$ |
| $v_{27}$ | a''  | 0.99781 1.00023 1.00054 | $c$ | 0.99816 1.00063 1.00086 | $c$ |
| $v_{28}$ | a''  | 1.00319 1.00070 1.00056 | $c$ | 0.99974 1.00026 1.00043 | $c$ |
| $v_{29}$ | a''  | 0.99495 0.99929 0.99902 | $c$ | 0.99279 1.00110 0.99903 | $c$ |

$A"=0.2887$ cm$^{-1}$, $B"=0.0785$ cm$^{-1}$, $C"=0.0624$ cm$^{-1}$, $A"'=0.2171$ cm$^{-1}$, $B"'=0.0916$ cm$^{-1}$, $C"'=0.0652$ cm$^{-1}$
| $v$ | Sym. | $a''$ | $A''/A''$ | $B'/B''$ | $C'/C''$ | type ratio | $A''/A''$ | $B'/B''$ | $C'/C''$ | type ratio |
|-----|------|-------|-----------|-----------|-----------|------------|-----------|-----------|-----------|------------|
| $v_1$ | $a'$   | 0.99904 | 0.99988 | 0.99962 | $a/b = 8/92$ | 0.99695 | 1.00052 | 0.99899 | $a/b = 13/87$ |
| $v_2$ | $a'$   | 0.99910 | 0.99888 | 0.99897 | $a/b = 75/25$ | 0.99958 | 0.99958 | 0.99960 | $a/b = 2/92$ |
| $v_3$ | $a'$   | 0.99875 | 1.00012 | 0.99963 | $a/b = 93/7$ | 1.00002 | 0.99953 | 0.99976 | $a/b = 99/1$ |
| $v_4$ | $a'$   | 0.99930 | 1.00015 | 0.99991 | $a/b = 50/50$ | 1.00004 | 0.99965 | 0.99987 | $a/b = 77/23$ |
| $v_5$ | $a'$   | 0.99965 | 0.99985 | 0.99992 | $a/b = 67/33$ | 0.99948 | 1.00002 | 0.99996 | $a/b = 48/52$ |
| $v_6$ | $a'$   | 1.00081 | 0.99765 | 0.99857 | $a/b = 2/98$ | 1.00094 | 0.99783 | 0.99915 | $a/b = 86/14$ |
| $v_7$ | $a'$   | 0.99906 | 1.00031 | 0.99992 | $a/b = 13/87$ | 0.99894 | 0.99864 | 0.99898 | $a/b = 99/1$ |
| $v_8$ | $a'$   | 0.99991 | 0.99967 | 1.00061 | $a/b = 62/38$ | 0.99921 | 0.99944 | 1.00060 | $a/b = 74/26$ |
| $v_9$ | $a'$   | 0.99566 | 0.99930 | 1.00049 | $a/b = 1/99$ | 0.99970 | 1.00026 | 0.99970 | $a/b = 99/1$ |
| $v_{10}$ | $a'$ | 0.99812 | 0.99790 | 0.99565 | $a/b = 39/61$ | 0.99980 | 0.99671 | 0.99766 | $a/b = 64/36$ |
| $v_{11}$ | $a'$ | 0.99778 | 0.99904 | 0.99755 | $a/b = 27/73$ | 1.00138 | 0.99962 | 0.99999 | $a/b = 97/3$ |
| $v_{12}$ | $a'$ | 1.00089 | 1.00045 | 0.99966 | $a/b = 5/95$ | 0.99863 | 0.99812 | 0.99731 | $a/b = 67/33$ |
| $v_{13}$ | $a'$ | 0.99930 | 1.00188 | 0.99933 | $a/b = 96/4$ | 1.00153 | 1.00116 | 0.99945 | $a/b = 92/8$ |
| $v_{14}$ | $a'$ | 0.99945 | 0.99673 | 0.99914 | $a/b = 91/9$ | 0.99944 | 0.99876 | 0.99892 | $a/b = 20/80$ |
| $v_{15}$ | $a'$ | 0.99923 | 0.99924 | 0.99903 | $a/b = 98/2$ | 0.99872 | 0.99874 | 0.99840 | $a/b = 1/99$ |
| $v_{16}$ | $a'$ | 0.99782 | 0.99961 | 0.99844 | $a/b = 96/4$ | 0.99913 | 0.99942 | 0.99850 | $a/b = 99/1$ |
| $v_{17}$ | $a'$ | 0.99979 | 0.99941 | 0.99920 | $a/b = 59/41$ | 0.99922 | 0.99910 | 0.99911 | $a/b = 72/28$ |
| $v_{18}$ | $a'$ | 1.00123 | 0.99981 | 0.99965 | $a/b = 44/56$ | 1.00025 | 1.00152 | 1.00082 | $a/b = 27/73$ |
| $v_{19}$ | $a'$ | 1.00128 | 1.00161 | 0.99945 | $a/b = 9/91$ | 1.00561 | 1.00069 | 0.99957 | $a/b = 91/9$ |
| $v_{20}$ | $a'$ | 1.00220 | 0.99995 | 0.99807 | $a/b = 52/48$ | 0.99666 | 1.00169 | 0.99645 | $a/b = 11/89$ |
| $v_{21}$ | $a''$ | 0.99987 | 0.99987 | 0.99994 | $c$ | 0.99946 | 1.00026 | 0.99999 | $c$ |
| $v_{22}$ | $a''$ | 1.00344 | 0.99967 | 1.00011 | $c$ | 0.99985 | 1.00264 | 1.00013 | $c$ |
| $v_{23}$ | $a''$ | 1.00060 | 1.00068 | 0.99997 | $c$ | 0.99957 | 0.99894 | 0.99974 | $c$ |
| $v_{24}$ | $a''$ | 0.99914 | 0.99934 | 0.99979 | $c$ | 0.99831 | 0.99907 | 0.99991 | $c$ |
| $v_{25}$ | $a''$ | 0.99749 | 0.99901 | 0.99992 | $c$ | 1.00013 | 0.99792 | 1.00032 | $c$ |
| $v_{26}$ | $a''$ | 0.99991 | 0.99939 | 1.00015 | $c$ | 0.99949 | 0.99961 | 1.00026 | $c$ |
| $v_{27}$ | $a''$ | 0.99896 | 1.00089 | 1.00106 | $c$ | 1.00348 | 0.99808 | 1.00157 | $c$ |
| $v_{28}$ | $a''$ | 0.99839 | 0.99794 | 1.00071 | $c$ | 0.99461 | 0.99943 | 1.00069 | $c$ |
| $v_{29}$ | $a''$ | 0.99079 | 1.00483 | 1.00274 | $c$ | 0.99619 | 1.00094 | 1.00129 | $c$ |
| $v_{30}$ | $a''$ | 0.99308 | 1.00021 | 0.99946 | $c$ | 1.00128 | 0.99783 | 1.00012 | $c$ |

$A''=0.1841$ cm$^{-1}$, $B''=0.0991$ cm$^{-1}$, $C''=0.0652$ cm$^{-1}$  
$A''=0.1582$ cm$^{-1}$, $B''=0.1214$ cm$^{-1}$, $C''=0.0696$ cm$^{-1}$
Supplementary Table 11. Comparison of observed vibrational wavenumbers of (Z)-C₂H₃C(CH₃)I (2) in region 800–1450 cm⁻¹ with those calculated with the B3LYP/aug-cc-pVTZ-pp method.

| Mode | Sym. | Experiment | Calculation | Mode description |
|------|------|------------|-------------|------------------|
|      |      | v/cm⁻¹     | v/cm⁻¹      |                  |
|      |      | Intensity  | Intensity   |                  |
|      |      |            | a           |                  |
| v₈   | a’   | 1406       | 1418        | C²H bend/C²C³ str. |
|      |      | 13         | 8.9         |                  |
| v₉   | a’   | 1379       | 1221        | C⁴H₃ umbrella    |
|      |      | 3.1        | 1.6         |                  |
| v₁₀  | a’   | 1261       | 1261        | C²/C³ str./C²H bend |
|      |      | 38         | 37.0        |                  |
| v₁₁  | a’   | 1221       | 1108        | C¹C² str.       |
|      |      | 1.6        | 35.3        |                  |
| v₁₂  | a’   | 1109       | 1108        | C³C⁴ str./C¹C²C³ bend |
|      |      | 100        | 35.3        |                  |
| v₁₃  | a’   | 1019       | 1018        | CH ip bend/C⁴H₂ wag |
|      |      | 22         | 7.5         |                  |
| v₁₄  | a’   | 873        | 887         | C¹H₂ ip bend/C³I str. |
|      |      | 16         | 10.3        |                  |
| v₂₀  | a”   | 1429       | 1030        | C⁴H₂ twist      |
|      |      | 11.0       | 10.4        |                  |
| v₂₁  | a”   | 1013       | 1030        | C⁴H₂ rock/C²C³C⁴ oop def. |
|      |      | 1.6        | 10.4        |                  |
| v₂₂  | a”   | 925        | 930         | C²H oop bend    |
|      |      | 8          | 10.4        |                  |
| v₂₃  | a”   | 803        |             | C¹H₂ wag        |
|      |      | 40.8       |             |                  |

a Harmonic vibrational wavenumber x scaled according to (0.9708 ± 0.0159)x + (9.3 ± 20.7); see text. b Percentage IR intensities relative to the most intense band near 1109 cm⁻¹. c In unit of km mol⁻¹. d Approximate mode description. str.: stretch; def.: deform; ip: in-plane; oop: out-of-plane.
Supplementary Table 12. Comparison of observed vibrational wavenumbers of syn-trans-C_2H_3C(CH_3)OO (3) in region 800–1500 cm\(^{-1}\) with those calculated with the B3LYP/aug-cc-pVTZ method.

| Mode | Sym. | Experiment \(\nu /\text{cm}^{-1}\) | Int.\(^b\) | Harmonic\(^a\) \(\nu /\text{cm}^{-1}\) | Int.\(^c\) | Anharmonic \(\nu /\text{cm}^{-1}\) | Mode description\(^d\) |
|------|------|---------------------------------|---------|---------------------------------|---------|---------------------------------|-------------------------|
| \(v_7\) | a’   | 1455                            | 14.6    | 1445                            |         | 1437                            | asym. C(2)C(3)C(4) str. |
| \(v_8\) | a’   | 1454                            | 22.3    |                                 |         |                                 | C(3)O str.               |
| \(v_9\) | a’   | 1416                            | 12      | 1425                            | 15.3    | 1420                            | C(1)H_2 scissor          |
| \(v_{10}\) | a’   | 1346                            | 7       | 1367                            | 18.2    | 1365                            | C(4)H_3 umbrella         |
| \(v_{11}\) | a’   | 1304                            | 6.5     | 1308                            |         |                                 | C(2)C(3) str./HC(1)C(2) bend |
| \(v_{12}\) | a’   | 1278                            | 1.3     | 1282                            |         |                                 | C(2)H ip bend           |
| \(v_{13}\) | a’   | 1060                            | 45      | 1045                            | 34.5    | 1048                            | CH ip bend/C(4)H_3 wag   |
| \(v_{14}\) | a’   | 987                             | 44      | 1000                            | 32.4    | 1004                            | CH ip bend               |
| \(v_{15}\) | a’   | 948                             | 100     | 948                             | 127.4   | 947                             | OO str.                  |
| \(v_{16}\) | a’   | 792                             | 0.1     | 791                             |         |                                 | sym. C(2)C(3)C(4) str.  |
| \(v_{22}\) | a''  | 1383                            | 10      | 1409                            | 8.9     | 1396                            | C(4)H_3 def.            |
| \(v_{23}\) | a''  | 1020                            | 0.1     | 1033                            |         |                                 | oop def.                 |
| \(v_{24}\) | a''  | 1004                            | 16.9    | 951                             |         |                                 | C(2)H oop bend          |
| \(v_{25}\) | a''  | 916/908                         | 15      | 948                             | 43.6    | 939                             | C(1)H_2 wag             |

\(^a\)Harmonic vibrational wavenumber \(x\) scaled according to \((0.9708 \pm 0.0159) x + (9.3 \pm 20.7)\); see text. \(^b\)Percentage IR intensities relative to the most intense band near 948 cm\(^{-1}\). \(^c\)In unit of km mol\(^{-1}\). \(^d\)Approximate mode description. str.: stretch; def.: deform; ip: in-plane; oop: out-of-plane.
Supplementary Table 13. Comparison of observed vibrational wavenumbers of syn-cis-C$_2$H$_3$C(CH$_3$)OO in region 800–1500 cm$^{-1}$ with those calculated with the B3LYP/aug-cc-pVTZ method.

| Mode | Sym. | Experiment \( \nu / \text{cm}^{-1} \) | Harmonic$^a$ \( \nu / \text{cm}^{-1} \) | Int.$^b$ | Anharmonic \( \nu / \text{cm}^{-1} \) | Mode description$^c$ |
|------|------|---------------------------------|----------------|--------|----------------|---------------------|
| \( \nu_7 \) | a’ | 1460 | 19.7 | 1440 | C(3)O str. |
| \( \nu_8 \) | a’ | 1452 | 48.1 | 1449 | asym. C(2)C(3)C(4) str. |
| \( \nu_9 \) | a’ | 1403 | 0.1 | 1394 | C(1)H$_2$ scissor/ C(4)H$_3$ umbrella |
| \( \nu_{10} \) | a’ | 1366 | 23.3 | 1364 | C(4)H$_3$ umbrella |
| \( \nu_{11} \) | a’ | 1308 | 0.4 | 1319 | C(1)H/C(2)H iph. bend |
| \( \nu_{12} \) | a’ | 1243 | 26.5 | 1239 | C(2)C(3) str./C(2)H ip bend |
| \( \nu_{13} \) | a’ | 1084 | 9.2 | 1086 | CH ip bend |
| \( \nu_{14} \) | a’ | 1011 | 12.3 | 1010 | C(4)H$_3$ wag/CH ip bend |
| \( \nu_{15} \) | a’ | 935 | 85.5 | 934 | OO str. |
| \( \nu_{16} \) | a’ | 794 | 2.1 | 792 | sym. C(2)C(3)C(4) str. |
| \( \nu_{22} \) | a’ | 1408 | 9.8 | 1393 | C(4)H$_3$ def. |
| \( \nu_{23} \) | a’ | 1031 | 8.9 | 1017 | oop def. |
| \( \nu_{24} \) | a’ | 999 | 12.4 | 947 | C(2)H oop bend |
| \( \nu_{25} \) | a’ | 980 | 33.9 | 968 | C(1)H$_2$ wag |

$^a$Harmonic vibrational wavenumber \( \nu \) scaled according to \((0.9708 \pm 0.0159) \times (9.3 \pm 20.7)\); see text. $^b$In unit of km mol$^{-1}$. $^c$Approximate mode description. str.: stretch; def.: deform; ip: in-plane; oop: out-of-plane; iph: in-phase. $^d$Overlapped with syn-trans-MVKO.
Supplementary Table 14. Comparison of observed vibrational wavenumbers of C$_2$H$_3$C(CH$_3$)IOO (4) in region 800‒1500 cm$^{-1}$ with C$_2$H$_3$C(CH$_3$)IOO-1 and C$_2$H$_3$C(CH$_3$)IOO-2 calculated with the B3LYP/aug-cc-pVTZ-pp method.

| Mode | Experiment | C$_2$H$_3$C(CH$_3$)IOO-1$^a$ | C$_2$H$_3$C(CH$_3$)IOO-2$^a$ | Mode description$^d$ |
|------|------------|----------------------------|----------------------------|---------------------|
| v$_8$ | 1457 4.3 | 1455 4.9 | C$^4$H$_3$ def. |
| v$_9$ | 1452 2.7 | 1442 2.1 | C$^4$H$_3$ def. |
| v$_{10}$ | 1421 15.7 | 1422 13.2 | C$^1$H$_2$ scissor |
| v$_{11}$ | 1375 53 | 1376 15.4 | C$^4$H$_3$ umbrella |
| v$_{12}$ | 1305 0.1 | 1304 0.1 | HC$^2$C$^1$ bend |
| v$_{13}$ | 1213 53 | 1247 9.3 | C$^2$C$^3$ str. |
| v$_{14}$ | 1145 4.2 | 1170 14.0 | OO str. |
| v$_{15}$ | 1108 100 | 1108 31.7 | 1103 10.2 | CH ip bend/C$^4$H$_2$ wag |
| v$_{16}$ | 1063 80 | 1054 56.8 | 1050 74.7 | C$^3$C$^4$ str./C$^4$H$_2$ wag |
| v$_{17}$ | 1008 13.4 | 1020 10.0 | C$^2$H oop bend |
| v$_{18}$ | 986 47 | 985 3.6 | 1002 8.2 | CH ip bend/C$^4$H$_2$ wag |
| v$_{19}$ | 954 39.3 | 956 37.3 | C$^1$H$_2$ wag |
| v$_{20}$ | 885 100 | 847 11.4 | 870 7.3 | C$^2$C$^3$ str. |

$^a$Harmonic vibrational wavenumber $x$ scaled according to $(0.9708 \pm 0.0159) x + (9.3 \pm 20.7)$; see text. $^b$Percentage IR intensities relative to the most intense band near 1109 cm$^{-1}$. $^c$In unit of km mol$^{-1}$. $^d$Approximate mode description. str.: stretch; def.: deform; ip: in-plane; oop: out-of-plane.
## Supplementary Table 15. Summary on estimates of concentrations of species in varied experiments.

| Description                                                                 | Unit       | Expt. 1 | Expt. 2 | Expt. 3 | Expt. 4 |
|-----------------------------------------------------------------------------|------------|---------|---------|---------|---------|
| 1 Pressure of (Z)-(CH₂I)HC=C(CH₃)I (1)                                      | mTorr      | 40      | 40      | 35      | 42      |
| 2 Pressure of O₂                                                            | Torr       | 35      | 82      | 246     | 347     |
| 3 Probed period                                                             | µs         | 0‒5     | 0‒5     | 0‒5     | 12.5‒25 |
| 4 Integrated absorbance 1130–1190 cm⁻¹ for (1)                             | cm⁻¹       | 0.35    | ± 0.02a | 0.33    | ± 0.02  | 0.11    | ± 0.01  | 0.081   | ± 0.004 |
| 5 Integrated absorbance, B₆ (920–960 cm⁻¹) for (3)                          | cm⁻¹       | 0.12    | ± 0.01  | 0.10    | ± 0.01  | 0.028   | ± 0.002 | 0.17    | ± 0.001 |
| 6 Integrated absorbance, C₃ (1100–1120 cm⁻¹) for (4)                        | cm⁻¹       | 0.021   | ± 0.002 | 0.019   | ± 0.002 | 0.011   | ± 0.001 | 0.009   | ± 0.001 |
| 7 Integrated absorbance, C₆ (862–907 cm⁻¹) for (4)                          | cm⁻¹       | 0.027   | ± 0.003 | 0.025   | ± 0.003 | 0.015   | ± 0.002 | 0.018b  | ± 0.002 |
| 8 Loss of (1) from raw 4 upon irradiation                                   | 10¹³c      | 34      | ± 2d    | 32      | ± 2     | 11      | ± 1     | 7.9     | ± 0.4   |
| 9 (3) after irradiation, from row 5                                          | 10¹³c      | 9.6     | ± 1     | 8.0     | ± 0.8   | 2.2     | ± 0.2   | 1.4     | ± 0.1   |
| 10 (4) after irradiation, from row 6                                         | 10¹³c      | 10.5    | ± 1.0   | 9.5     | ± 1.0   | 5.5     | ± 0.6   | 4.5     | ± 0.5   |
| 11 (4) from after irradiation, row 7                                         | 10¹³c      | 15.4    | ± 1.7   | 14.3    | ± 1.7   | 8.6     | ± 1.1   | 10.3b   | ± 1.1   |
| 12 (3) from rows 8 & 9, relative to experiment 1                             | 1.00       | ± 0.15e | 0.89    | 0.71    | ± 0.12  | 0.63    | ± 0.09  |         |
| 13 (4) from rows 8 & 10, relative to experiment 1                            | 1.00       | ± 0.16  | 0.96    | 1.62    | ± 0.29  | 1.84    | ± 0.30  |         |
| 14 (4) from rows 8 & 11s, relative to experiment 1                           | 1.00       | ± 0.18  | 0.97    | 1.73    | ± 0.35  | 2.87b   | ± 0.49  |         |

*Error bars reflect mainly uncertainties in baseline. *b*Might be interfered by an unknown band appeared at high pressure. *c*In unit of molecule cm⁻³. *d*Error bars reflect only the error from integration, but not the error due to interference of other species, which is difficult to estimate. *e*Error bars reflect propagated errors from numbers in two rows.
Supplementary Fig. 1 Geometries of conformers of methyl vinyl ketone oxide (MVKO) and dioxole predicted with the B3LYP/aug-cc-pVTZ method. (a) syn-trans-$\text{C}_2\text{H}_3\text{C}(\text{CH}_3)\text{OO}$ (3). (b) syn-cis-$\text{C}_2\text{H}_3\text{C}(\text{CH}_3)\text{OO}$. (c) anti-trans-$\text{C}_2\text{H}_3\text{C}(\text{CH}_3)\text{OO}$. (d) anti-cis-$\text{C}_2\text{H}_3\text{C}(\text{CH}_3)\text{OO}$. (e) dioxole. Bond lengths (black) are in Å and angles (blue) are in degree; $\Phi$ is the dihedral angle.
Supplementary Fig. 2 Geometries of precursors (Z)-(E)-(CH2I)HC=C(CH3)I and (Z)-(E)- iodoalkyl radicals C2H3C(CH3)I and (CH2I)CHC(CH3) predicted with the B3LYP/aug-cc-pVTZ-pp method. (a) (Z)-(CH2I)HC=C(CH3)I. (b) (E)-(CH2I)HC=C(CH3)I. (c) (Z)-C2H3C(CH3)I. (d) (E)-C2H3C(CH3)I. (e) (Z)-(CH2I)CHC(CH3). (f) (E)-(CH2I)CHC(CH3). Bond lengths (black) are in Å and angles (blue) are in degree; \( \Phi \) is the dihedral angle.
Supplementary Fig. 3 Geometries of nine conformers of iodoperoxy radicals $C_2H_5C(CH_3)IOO$ predicted with the B3LYP/aug-cc-pVTZ-pp method. Bond lengths (black) are in Å and angles (blue) are in degree; $\Phi$ is the dihedral angle.
Supplementary Fig. 4 Geometries of six conformers of iodoperoxy radicals C(CH₃)ICHCH₂OO predicted with the B3LYP/aug-cc-pVTZ-pp method. Bond lengths (black) are in Å and angles (blue) are in degree; Φ is the dihedral angle.
Supplementary Fig. 5 Comparison of IR spectra of (Z)-CH$_2$IHC=C(CH$_3$)$_2$ (1) in the gaseous phase and in solid $p$-H$_2$ with quantum-chemical calculations. (a) Gaseous spectrum. (b) spectrum in solid $p$-H$_2$. (c) stick IR spectrum predicted with the B2PLYP-D3/aug-cc-pVTZ-pp method. (d) stick IR spectrum predicted with the B3LYP/aug-cc-pVTZ-pp method.
Supplementary Fig. 6 Temporal evolution of observed spectra and processed spectra in region 1450‒850 cm\(^{-1}\) at resolution 1.0 cm\(^{-1}\) upon photolysis at 248 nm of a flowing mixture of (Z)-1,3-diiodobut-2-ene/N\(_2\) (0.03/75 Torr) and comparison with predicted stick spectra. (a) Absorption spectrum before photolysis. (b) Difference spectrum recorded 0‒3 µs after photolysis. (c) Expanded spectrum of (b) with negative bands truncated. (d) Expanded difference spectrum recorded 10‒15 µs after photolysis. (e) Spectrum of (c) with absorption bands of precursor (1) added back to eliminate negative bands. Grey areas in (c)–(e) represent regions of possible interference from the absorption of precursor (1). New features in group A are marked A\(_1\)–A\(_6\).
Supplementary Fig. 7 Comparison of IR spectra of (Z)-C₂H₃C(CH₃)I (2) in the gaseous phase with quantum-chemical calculations. (a) (Z)-C₂H₃C(CH₃)I in the gaseous phase. (b) Stick IR spectrum of (Z)-C₂H₃C(CH₃)I. (c) Stick IR spectrum of (E)-C₂H₃C(CH₃)I predicted with the B3LYP/aug-cc-pVTZ-pp method. Grey areas represent regions of possible interference from absorption of the parent molecules.
Supplementary Fig. 8 Temporal evolution of observed and processed spectra in region 1450‒850 cm⁻¹ at resolution 0.5 cm⁻¹ upon photolysis at 248 nm of a flowing mixture of (Z)-1,3-diiodo-but-2-ene/O₂ (0.04/35 Torr). Difference spectra recorded 0‒5 µs (a), 5–10 µs (b), and 30–35 µs (c) after irradiation; the absorption of the precursor is shown on a reduced scale and shifted upward in (a). (d) Spectrum of (Z)-C₂H₃C(CH₃)I (2) taken from Supplementary Figure 6(e). (e) Absorption spectrum of methyl vinyl ketone (MVK); (f)‒(h) processed spectra of (a)‒(c) with bands of (2) and MVK removed and those of the precursor (1) added back. Grey areas represent regions of possible interference from absorption of the parent molecules. New features are marked B₁–B₇ in (g).
(a) Major resonance structures of MVKO

(b) Frontier-orbital diagrams showing the delocalization over the CCCOO skeleton

Supplementary Fig. 9 Resonance structures and frontier orbitals of syn-trans-MVKO. The electron density isovalues are 0.01 e/Å³.
Supplementary Fig. 10 Temporal evolution of observed and processed spectra in region 1450‒850 cm⁻¹ at resolution 1.0 cm⁻¹ upon photolysis at 248 nm of a flowing mixture of (Z)-1,3-diiodo-but-2-ene/O₂ (0.042/347 Torr). Difference spectra recorded 0‒25 µs (a), 25‒50 µs (b), and 50‒100 µs (c) after irradiation; the absorption of the precursor is shown on a reduced scale in (a). (d) Spectrum of MVKO (3) taken from Figure 3(a) of main text. (e) Absorption spectrum of methyl vinyl ketone (MVK). (f)‒(h) processed spectra of (a)‒(c) with bands of (3) and MVK removed and those of the precursor (1) added back. Grey areas represent regions of possible interference from absorption of the parent molecules. New features are marked C₁‒C₆ in (f).
Supplementary Fig. 11 Temporal evolution of observed and processed spectra in region 1450–850 cm\(^{-1}\) at resolution 1.0 cm\(^{-1}\) upon photolysis at 248 nm of a flowing mixture of (Z)-1,3-diiodo-but-2-ene/O\(_2\) (0.035/236 Torr). Difference spectra recorded 0–10 \(\mu\)s (a), 10–20 \(\mu\)s (b), and 20–30 \(\mu\)s (c) after irradiation; the absorption of the precursor is shown on a reduced scale in (a). (d) Spectrum of MVKO (3) taken from Figure 3(a) of main text. (e) Absorption spectrum of methyl vinyl ketone (MVK). (f)–(h) processed spectra of (a)–(c) with bands of (3) and MVK removed and those of the precursor (1) added back. Grey areas represent regions that might suffer interference from absorption of the parent molecules. New features are marked \(C_1\)–\(C_6\) in (f).
Supplementary Fig. 12 Comparison of bands in group C with stick IR spectra of nine conformers of iodoperoxy radical $\text{C}_2\text{H}_3\text{C}(\text{CH}_3)\text{IOO}$. (a) Spectrum taken from Supplementary Figure 10(g); grey areas represent regions of possible interference from absorption of the precursor. (b)–(j) Stick spectra of nine conformers simulated according to scaled harmonic vibrational wavenumbers and IR intensities calculated with the B3LYP/aug-cc-pVTZ-pp method.
Supplementary Fig. 13 Comparison of bands in group C with stick IR spectra of six conformers of iodoperoxy radical C(CH₃)ICCH₂OO. (a) Spectrum taken from Supplementary Figure 10(g); grey areas represent regions of possible interference from absorption of the precursor. (b)–(g) Stick spectra of six conformers simulated according to scaled harmonic vibrational wavenumbers and IR intensities calculated with the B3LYP/aug-cc-pVTZ-pp method.
Supplementary Fig. 14 Temporal profiles of species upon photolysis at 248 nm of a mixture of (Z)-(CH₂I)HC=C(CH₃)I (0.04 Torr) and O₂ (35 Torr) and a mixture of (Z)-(CH₂I)HC=C(CH₃)I (0.04 Torr) and O₂ (347 Torr). (a) Criegee intermediate MVKO (3) integrated over region 920–960 cm⁻¹ (blue circles, B₆ band) and iodoalkyl radical (2) integrated over region 1260–1270 cm⁻¹ (black triangles). (b) MVKO (3) (blue circles), iodoperoxy adduct (4) integrated over 1100–1120 cm⁻¹ (black triangle, C₃ band) and 862–907 cm⁻¹ (red inverted triangle, C₆ band), and methyl vinyl ketone (MVK) integrated over 1250–1270 cm⁻¹ (pink diamonds).
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