Supporting Information
Four-Carbon Criegee Intermediate from Isoprene Ozonolysis: Methyl Vinyl Ketone Oxide Synthesis, Infrared Spectrum, and OH Production

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S1. Synthesis of MVK-OO

## S1.1. Synthesis of Precursor

Initially, a Z/E mixture of 1,3-diiodobut-2-ene was synthesized following the general procedure of Manickam et al. ${ }^{1}$, as shown in Scheme S1A. Anhydrous zinc chloride ( $0.290 \mathrm{~g}, 2.13 \mathrm{mmol}$, Sigma Aldrich, $\geq 98 \%$ ) was added under a nitrogen atmosphere to a solution of but-2-yn-1-ol (1.00 g, 14.2 mmol , Alfa Aesar, 98\%) in dry dichloromethane (10 mL). In a dark fume hood, the colorless heterogeneous mixture was wrapped with aluminum foil and cooled to $-40^{\circ} \mathrm{C}$ using an acetonitrile/dry ice bath for 15 min. Trimethylsilyl iodide (TMSI, $4.40 \mathrm{~mL}, 31.2 \mathrm{mmol}$, Alfa Aesar, 97\%) was added dropwise over a period of 40 min. After the addition was complete, the reaction mixture was warmed to $0^{\circ} \mathrm{C}$ by replacing the acetonitrile/dry ice bath with an ice bath and the reaction mixture was stirred for 1 h . After 1 h , the mixture was allowed to warm to room temperature (rt) by removing the ice bath and the solution was stirred for 16 h . The crude product was filtered over a bed of Celite, and the Celite was then washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 20 \mathrm{~mL})$ and concentrated in vacuum. The crude product was then redissolved in $\mathrm{CH}_{2} \mathrm{Cl}_{2}(15$ mL ) and washed with saturated $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}(2 \mathrm{x} 10 \mathrm{~mL})$. The organic layer was concentrated in vacuum to yield a dark brown oil. The product was further purified via column chromatography on silica gel (hexanes: $\mathrm{Et}_{2} \mathrm{O}=20: 1$ ) and then vacuum distilled $\left(67-69^{\circ} \mathrm{C} / 50 \mathrm{mTorr}\right)$ to yield a brown oil $(1.30 \mathrm{~g}, 30 \%$ yield, $Z / E \sim 10 / 1$ ). The ${ }^{1} \mathrm{H}$ NMR spectrum matched the previously published literature data for Z-1,3-diiodobut-2-ene. ${ }^{2}{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): (Z)-1,3-diiodobut-2-ene $\delta 5.7(\mathrm{q}, 1 \mathrm{H}), 3.9(\mathrm{~d}, 2 \mathrm{H})$, $\delta 2.5(\mathrm{~d}, 3 \mathrm{H}) .(E)-1,3$-diiodobut-2-ene $\delta 6.0(\mathrm{q}, 1 \mathrm{H}), 4.4(\mathrm{~d}, 2 \mathrm{H}), \delta 1.7(\mathrm{~d}, 3 \mathrm{H})$.

In a modified procedure, $(Z / E)$-1,3-diiodobut-2-ene was synthesized in higher yield by optimizing the procedure of Gras et al. ${ }^{3}$ that does not require a zinc chloride catalyst, as shown in Scheme S1B. But-2-yn-1-ol (0.54 mL, 7.13 mmol , Alfa Aesar, 98\%) was diluted in dry $\mathrm{Et}_{2} \mathrm{O}(10 \mathrm{~mL})$. In a dark fume hood, the homogeneous mixture was wrapped with aluminum foil and cooled to $-40^{\circ} \mathrm{C}$ with an acetonitrile/dry ice bath for 15 min . TMSI ( $2.23 \mathrm{~mL}, 15.6 \mathrm{mmol}$, Alfa Aesar, 97\%) was added dropwise and with rapid stirring over a period of 30 min. Following addition of TMSI, the reaction mixture was
allowed to warm to room temperature, stirred for 1 h , and quenched with a saturated $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ solution (10 mL ). A $Z / E$ mixture of the 1,3-diiodobut-2-ene product was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 15 \mathrm{~mL})$. The combined organic phases were washed with a brine solution ( 15 mL ), dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$ and concentrated under vacuum. The product was purified via column chromatography on silica gel (hexanes: $\mathrm{Et}_{2} \mathrm{O}=20: 1$ ) to yield a brown oil ( $1.85 \mathrm{~g}, 84 \%$ yield, $Z / E \sim 5 / 1$ ). Further purification was conducted to obtain a high quality NMR spectrum via column chromatography on silica gel eluted with hexanes to yield a yellow oil (Z/E ~ 14:1). For (Z)-1,3-diiodobut-2-ene ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 5.7(\mathrm{q}, 1 \mathrm{H}), 3.9(\mathrm{~d}, 2 \mathrm{H}), \delta 2.5$ (d, 3H) which is consistent with previous published literature data. ${ }^{2}{ }^{13} \mathrm{C}\left({ }^{1} \mathrm{H}\right) \mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ 132.1, 106.9, 33.7, 9.4. For (E)-1,3-diiodobut-2-ene ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 6.0(\mathrm{q}, 1 \mathrm{H}), 4.4(\mathrm{~d}$, 2H), 1.7 (d, 3H). ${ }^{13} \mathrm{C}\left({ }^{1} \mathrm{H}\right)$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 134.6, 105.5, 22.7, 18.6. HRMS (EI): m/z calculated for (Z/E)-1,3-diiodobut-2-ene 307.8559, observed 307.8560 . The full ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra are shown in Figure S1.
(Z/E)-1,3-diiodobut-2-ene was further characterized via UV-Vis spectroscopy. The UV-Vis of $\mathrm{CH}_{2} \mathrm{I}_{2}$ was also acquired in a separate experiment. Dilute solutions of (Z/E)-1,3-diiodobut-2-ene (0.07 $\mathrm{mmol} / \mathrm{L})$ and $\mathrm{CH}_{2} \mathrm{I}_{2}(0.19 \mathrm{mmol} / \mathrm{L})$ in hexanes were prepared and the UV-Vis spectra shown in Figure S2 were recorded with a spectrophotometer (Jasco V-650). A previous study of the UV-Vis spectra of $\mathrm{CH}_{2} \mathrm{I}_{2}$ in both polar and nonpolar solvents indicated virtually no shift in peak absorption wavelengths compared to the gas phase UV spectrum. ${ }^{4}$ By analogy, the peak UV absorption of $(Z / E)-1,3$-diiodobut-2-ene in the gas phase is expected to be similar to that shown in hexanes solvent in Figure S2.

In addition, the FTIR spectrum of (Z/E)-1,3-diiodobut-2-ene on a KBr plate was obtained with an FTIR spectrometer (Thermo Scientific, Nicolet iS5), and is presented in Figure S3. A complementary theoretical calculation of the fundamental vibrational frequencies of (Z/E)-1,3-diiodobut-2-ene is given in a thesis. ${ }^{5}$ High frequency vibrations (ca. 2900-2960 $\mathrm{cm}^{-1}$ ) are assigned to the methyl CH stretches. CH scissor and CH wag vibrational modes appear in the $1000-1500 \mathrm{~cm}^{-1}$ energy region. The sharp feature at ca. $1630 \mathrm{~cm}^{-1}$ is attributed to the alkene $\mathrm{C}=\mathrm{C}$ stretch. The very strong C-I stretches appear at ca. $500 \mathrm{~cm}^{-1}$.

## S1.2. Oxygen Addition

As illustrated in Scheme 3 (main text), photolysis of the (Z/E)-1,3-diiodobut-2-ene precursor at 248 nm results in prompt dissociation to produce an internally excited allylic monoiodoalkene radical Int(1). Its subsequent reaction with $\mathrm{O}_{2}$ is expected to transiently form an iodoalkene peroxy radical intermediate $\operatorname{Int}(2)$.

Theoretical calculations were undertaken to map out C-O distinguished coordinate minimum energy paths (MEPs) for additions of $\mathrm{O}_{2}$ to both $\mathrm{C}_{(1)}$ and $\mathrm{C}_{(3)}$ radical sites of $\operatorname{Int}(1)$ at the CASPT2(9e,7o)/CBS(TZ,QZ)//CASPT2/cc-pVDZ level as shown in Figure S4. For the C and H atoms we employed Dunning's correlation consistent basis sets (cc-pVnZ), ${ }^{6}$ while for the I atom we employed the cc-pVnZ-PP relativistic pseudo-potential versions of these. ${ }^{7}$ The ( $9 \mathrm{e}, 7 \mathrm{o}$ ) active space for these calculations correlates with the $(3 \mathrm{e}, 3 \mathrm{o}) \pi$-space of the $\mathrm{C}_{4} \mathrm{H}_{6} \mathrm{I}$ radical coupled with the $(6 \mathrm{e}, 4 \mathrm{o}) \pi$-space of the $\mathrm{O}_{2}$ radical. An IPEA shift ${ }^{8}$ of 0.25 was employed. A related study of the addition of $\mathrm{O}_{2}$ to propargyl radical ${ }^{9}$ indicated that such an IPEA shifted CASPT2 approach provides a reliable prediction of the shape of the MEP for an oxygen molecule adding to a resonantly stabilized radical.

The calculated MEPs suggests that the addition of $\mathrm{O}_{2}$ to $\mathrm{C}_{(3)}$ will be both energetically and kinetically favored as illustrated in Figure S4. The bulky I atom at $\mathrm{C}_{(3)}$ might be expected to lead to some steric reduction in the rate for addition to $\mathrm{C}_{(3)}$ relative to that for $\mathrm{C}_{(1)}$. However, a scan of the torsional potentials (shown in Figure S5) suggests that there is actually greater steric hindrance for addition at the $\mathrm{C}_{(1)}$ site.

S2. Photoionization of 1,3-diiodobut-2-ene precursor and MVK-OO Criegee intermediate
The (Z/E)-1,3-diiodobut-2-ene precursor and photolytically generated MVK-OO Criegee intermediate were detected by photoionization using 10.5 eV (118 nm) vacuum ultraviolet (VUV) radiation with a Wiley-McLaren linear time-of-flight mass spectrometer (TOF-MS, RM Jordan). ${ }^{10}$ The 118 nm VUV radiation is generated by frequency-tripling the focused ( $\mathrm{f}=30 \mathrm{~cm}$, UV fused silica lens) third harmonic output ( $355 \mathrm{~nm}, 40 \mathrm{~mJ} / \mathrm{pulse}$ ) of an Nd:YAG laser (Continuum Powerlite 9010) in a
phase-matched $\mathrm{Xe} / \mathrm{Ar}(\sim 1: 10)$ cell, as described previously. ${ }^{11-13}$ The VUV is refocused ( $\mathrm{f}=20, \mathrm{MgF}_{2}$ lens) at the center of the interaction region in a TOF-MS. The residual 355 nm is spatially separated from the VUV utilizing the difference in their focal properties.

Photoionization of the (Z/E)-1,3-diiodobut-2-ene precursor is observed on the $\mathrm{m} / \mathrm{z}=308$ parent mass channel as shown in the upper panel of Figure S6. Several other fragment mass channels including I $(\mathrm{m} / \mathrm{z}=127), \mathrm{C}_{4} \mathrm{H}_{6} \mathrm{I}(\mathrm{m} / \mathrm{z}=181)$, and $\mathrm{I}_{2}(\mathrm{~m} / \mathrm{z}=254)$ are observed. A small signal at the $\mathrm{m} / \mathrm{z}=85$ mass channel is attributed to photoionization of dichloromethane (DCM), which is a solvent used in the synthetic procedure. The lower panel of Figure S6 shows the TOF mass spectrum obtained when 248 nm excimer radiation is introduced to photolyze the precursor in a $20 \% \mathrm{O}_{2} / \mathrm{Ar}$ gas mixture within the quartz capillary reactor tube prior to VUV photoionization. The diiodoalkene parent mass channel ( $\mathrm{m} / \mathrm{z}=308$ ) is reduced and the I fragment mass channel ( $\mathrm{m} / \mathrm{z}=127$ ) is noticeably enhanced. The inset displays the new $m / z=86$ mass channel attributed to the MVK-OO Criegee intermediate, which is not present in the absence of 248 nm photolysis.

Vertical ionization energies (VIE) and adiabatic ionization energies (AIE) for the four MVK-OO conformers are computed at the CCSD(T)-F12/CBS(TZ-F12,QZ-F12)//B2PLYP-D3/cc-pVTZ level of theory. The computed ionization energies of ca. $8.5-8.8 \mathrm{eV}$ for the four MVK-OO conformers (see Table S1) are ca. 2 eV lower than the 10.5 eV photon energy used for ionization, indicating that all four conformers of MVK-OO should be detected.

There are several possible isomers of MVK-OO $\left(\mathrm{C}_{4} \mathrm{H}_{6} \mathrm{O}_{2}\right)$ that could potentially be formed in the capillary reactor tube, collisionally stabilized, and contribute to the photoionization signal at $\mathrm{m} / \mathrm{z}=86$. 2-hydroperoxybuta-1,3-diene (HPBD, 1b) could be formed upon 1,4 H-atom transfer of syn-MVK-OO and stabilized prior to dissociation (see Sec. 3.1). 1-Hydroxybut-3-en-2-one (HB, 3) could be formed from HPBD via a roaming mechanism (see Sec. 4.1). In addition, dioxole (11), 3-oxobutanal ( $\beta$-dicarbonyl, 13), and various enol tautomers of dicarbonyl (e.g., enol, 14) could be formed via unimolecular rearrangement of anti-MVK-OO and stabilized prior to further reaction. There is also a possibility that
dioxole could arise from addition of $\mathrm{O}_{2}$ to the monoiodoalkene radical following photolysis of the (Z/E)-1,3-diiodobutene precursor as shown in Scheme S2. The computed ionization energies for possible isomers of MVK-OO are given in Table S1. If these species are stabilized, they can be ionized by 10.5 eV radiation and contribute to the observed photoionization signal. Future experiments are planned at the Advanced Light Source utilizing tunable VUV radiation that can distinguish between different isomers via their ionization thresholds.

On the other hand, IR transitions of other possible isomers of $\mathrm{C}_{4} \mathrm{H}_{6} \mathrm{O}_{2}$ are not expected to contribute to the IR action spectrum in the CH overtone region (Figure 4). The other isomers are more stable than MVK-OO and will not lead to OH products at the excitation energies used in this work (see Tables S2, S3 and S5). In addition, the computed IR absorption spectra of other isomers, e.g. HPBD (1a and 1b) and dioxole (11) (Figure S9), differ substantially from the observed IR action spectrum (Figure 4). For example, $\operatorname{HPBD}$ (1a and 1b) lacks CH overtone transitions below $5950 \mathrm{~cm}^{-1}$, while dioxole lacks CH overtone transitions in the 5850 to $5950 \mathrm{~cm}^{-1}$ region. Thus, IR action spectroscopy provides additional selectivity compared to IR absorption spectroscopy since only vibrationally excited molecules that release OH products are detected.

S3. Details of electronic structure calculations

## S3.1. Single Reference Calculations

Most of the energies for stationary points reported herein are calculated using the ANL0-B2F approach, which is slightly modified from the previously reported ANL0-F12 approach. ${ }^{14}$ It involves the determination of the CCSD(T)-F12/CBS-F12(TZ-F12,QZ-F12)//B2PLYP-D3/cc-pVTZ electronic energies, together with corrections for higher order electronic excitations (evaluated at the CCSDT(Q)/ccpVDZ level), core-valence interactions (evaluated at the $\operatorname{CCSD}(\mathrm{T}) / \mathrm{CBS}(\mathrm{TZ}, \mathrm{QZ})$ level using the ccpcVTZ and cc-pcVQZ basis sets), ${ }^{15}$ CCSD(T)/aug-cc-pcVTZ-DK Douglas-Kroll relativistic corrections, ${ }^{16}$ and B2PLYP-D3/cc-pVTZ vibrational perturbuation theory estimates for the zero-point energy. OH spin-
orbit corrections are also included. The ANL0-B2F stationary point energies are summarized in Table S2 together with the various components of the calculations.

For the species reported in Table S2, the T1 diagnostics are reasonably small, with the largest values for the MVK-OO isomers $(\sim 0.036)$ and for the transition states connecting the four MVK-OO isomers to the dioxirane species ( $\sim 0.039$ ). T1 diagnostics larger than 0.03 are indicative of significant multireference effects. However, the CCSDT(Q) correction can generally account for the multireference effects that might be expected for T 1 diagnostics in the 0.03 to 0.04 range. Our prior joint theoryexperiment studies ${ }^{17-20}$ of the kinetics and dynamics of the decomposition of a range of Criegee intermediates indicate that the inclusion of the CCSDT(Q)/cc-pVDZ correction within the ANL0 schemes results in accurate predictions of the barrier height for the H -transfer effecting the conversion from a CI to a vinylhydroperoxide.

The CCSDT(Q) corrections are generally large in Table S2 because they are specified relative to the value for syn-trans-MVK-OO, which itself has significant multireference character. Nevertheless, it is worth noting that there is great variance in the $\operatorname{CCSDT}(\mathrm{Q})$ corrections with values ranging from -0.3 to $1.8 \mathrm{kcal} \mathrm{mol}^{-1}$. This large span demonstrates the importance of proceeding beyond the $\operatorname{CCSD}(\mathrm{T})$ level when aiming for errors below $1.5 \mathrm{kcal} \mathrm{mol}^{-1}$. The corrections decrease in magnitude from the harmonic ZPE ( -6.0 to $1.9 \mathrm{kcal} \mathrm{mol}^{-1}$ ), to the $\operatorname{CCSDT}(\mathrm{Q})\left(-0.3\right.$ to $\left.1.8 \mathrm{kcal} \mathrm{mol}^{-1}\right)$, to the core-valence ( -0.4 to 0.3 $\mathrm{kcal} \mathrm{mol}{ }^{-1}$ ), to the relativistic ( -0.1 to $0.2 \mathrm{kcal} \mathrm{mol}^{-1}$ ), and finally the anharmonic ZPE correction ( -0.2 to $\left.0.2 \mathrm{kcal} \mathrm{mol}^{-1}\right)$.

## S3.2. Multireference Calculations

To explore the energetics of the pathways where single reference methods are not appropriate (e.g. bond breaking pathways), we employ complete active space wave functions with both multireference second order perturbation theory (CASPT2) and multi-reference singles and doubles configuration interaction including a fixed Davidson correction for the effect of higher order excitations (MRCISD+Q). In a number of instances, we employ the multireference methods to estimate the splitting
between the ground electronic state and that for a high spin state at the same geometry. High level CCSD(T)/CBS estimates of the high spin-state energies then yield a route to high accuracy energies for the ground state. ${ }^{21}$

## S3.2.1. Unimolecular decay of HPBD

Multireference methods are necessary to accurately examine the energetics of the dissociation of HPBD, (1a and 1b) and the related roaming mechanism presented in Scheme 5. To examine this pathway, we have employed CASPT2 and MRCISD+Q calculations with a 6 electron, 6 orbital (6e,6o) active space. This active space correlates with the ( $5 \mathrm{e}, 5 \mathrm{5}$ ) $\pi$-space of 2 -oxybuta-1,3-diene (OBD, 2a and 2b) fragment and the radical orbital of the OH fragment. Extrapolations to the CBS limit were obtained from cc-pVTZ and cc-pVQZ evaluations, while the underlying rovibrational analyses were performed with the cc-pVTZ basis set. The CASPT2 calculations employ an IPEA shift.

A detailed summary of the predicted stationary point energies for this interaction between the OH and OBD (2a and $\mathbf{2 b}$ ) fragments is provided in Table S3. The entries in this table explore two further complications to these pathways. First, the long-range nature of the roaming dynamics leads to a near degeneracy of the singlet and triplet states in that region. Furthermore, the presence of degenerate electronic orbitals in the OH product results in another pair of singlet and triplet states also being nearly degenerate. Therefore, there is an effective electronic degeneracy of 8 for the dynamics in the roaming region. It is unclear to what extent these electronic states are coupled on the timescale of the dissociations and isomerizations. A second complication arises from the fact that the OBD fragment has both cis (2a) and trans (2b) torsional isomers. For simplicity, we present only the roaming pathway from the lower energy trans-HPBD (1b) conformer. Notably, the CCSD(T) method is directly applicable to the analysis of the triplet states. The good agreement between the $\operatorname{CCSD}(\mathrm{T}) / \mathrm{CBS}$ (performed at the CASPT2 geometries) and multireference predictions for the triplet state energies validates the present
multireference predictions for the singlet state energies (especially the CASPT2 values which are within $0.1 \mathrm{kcal} \mathrm{mol}^{-1}$ of the $\operatorname{CCSD}(\mathrm{T}) / \mathrm{CBS}$ values).

Related roaming induced isomerizations pathways were studied in the recent work of Kuwata and coworkers analyzing the kinetics of some methyl substituted Creigee intermediates. ${ }^{22}$ Their analysis was based on unrestricted density functional theory (M06-L) geometries and spin-flip coupled cluster ( $\mathrm{CCSD}(\mathrm{dT})$ ) energies. The present multi-reference based examinations provide more quantitative validation of their prediction of a key roaming channel. One minor difference in our predictions is that we find the HOOC torsional potential has a single minimum in the region of the transition state, as validated by a sequence of torsionally constrained transition state optimizations. In contrast, Kidwell et al. ${ }^{23}$ and Kuwata et al. ${ }^{22}$ both found a second torsional minimum for this transition state in related Criegee systems.

## S3.2.2. Syn to anti-MVK-OO torsional isomerization

One route for isomerizing between syn and anti-MVK-OO involves a torsional rotation about the CO bond. In the transition state for this torsional isomerization, the partial CO double bond is broken and the wave function has strong diradical character, which implies strong multireference character for this geometry. Here we employ a $(4 \mathrm{e}, 4 \mathrm{o})$ active space to explore the singlet-triplet splitting at the singlet torsional saddle point geometry. The active space for these CASPT2 and MRCISD+Q calculations consists of the two-diradical orbitals and the CC $\pi$-space of the vinyl group. CCSD(T)-F12b/cc-pVTZF12 calculations for the triplet state relative to the CI then connect these estimates for the single-triplet splitting to absolute estimates for the torsional saddle point energy. We also include a $1.5 \mathrm{kcal} \mathrm{mol}^{-1}$ shift to approximately account for the typical CCSDT(Q)/cc-pVDZ lowering of the CI energy. The resulting energies are summarized in Table S4 for torsional isomerizations from both cis and trans conformers of syn-MVKOO to anti-MVK-OO.

## S3.2.3. Dioxole Pathway

The formation of the dioxole (11) provides the lowest energy pathway for decomposition of anti-MVK-OO. The lowest energy pathway from dioxole (11) appears to involve OO fission to convert the 5membered dioxole ring to a diradical species (12), as shown in Scheme 8 of the main text. There are a number of essentially barrierless pathways for converting this diradical to closed shell species. Herein, we consider a representative pathway that may potentially lead to OH products.

The calculations again employed a $(4 \mathrm{e}, 4 \mathrm{o})$ active space (again consisting of the radical orbitals and the CC $\pi$-space) to obtain CASPT2 and MRCISD+Q based estimates of the saddle point energies for the first three of these paths. Then, CCSD(T)-F12b/cc-pVTZ-F12 energies of the triplet state of the diradical are combined with multi-reference spin-splitting estimates to obtain the final energy estimates tabulated in Table S5.

## S4. Spectral and kinetic analyses

A simulation of the rotational band contour for the strongest predicted IR transition of syn-trans-MVK-OO at $6200 \mathrm{~cm}^{-1}$ is shown in Figure S8. The simulation utilizes calculated rotational constants for the ground vibrational state of syn-trans-MVK-OO $\left(\mathrm{a}=0.29 \mathrm{~cm}^{-1}, \mathrm{~b}=0.079 \mathrm{~cm}^{-1}, \mathrm{c}=0.063 \mathrm{~cm}^{-1}\right)$, predicted transition type (a:b = 0.14:0.86), and a rotational temperature of 10 K . The linewidth is a convolution of a Gaussian laser linewidth of $0.15 \mathrm{~cm}^{-1}$ and an assumed Lorentzian linewidth of $1.7 \mathrm{~cm}^{-1}$ representing homogeneous line broadening due to intramolecular vibrational energy redistribution (IVR). The latter is based on the linewidth determined for syn- $\mathrm{CH}_{3} \mathrm{CHOO}$ in the same energy regime. ${ }^{24}$ The overall breadth is approximated by a $\sim 3 \mathrm{~cm}^{-1}$ FWHM Gaussian lineshape, which is used to represent the rotational band contour at 10 K in the computed IR spectra (Figure 4). The rotational band contour simulations are performed in PGOPHER. ${ }^{25}$

As described in the main text, the experimental rate of OH production following IR excitation of MVK-OO is obtained from direct time-domain measurements. A representative time profile is shown in Figure S10. The overall temporal profile is well-represented by a dual exponential function

$$
\begin{equation*}
F(t)=A\left(-\exp \left(-\left(k_{\text {rise }}+k_{\text {fall }}\right) t\right)+\exp \left(-k_{\text {fall }} t\right)\right) \tag{S1}
\end{equation*}
$$

where $k_{\text {rise }}$ is the rate constant for the appearance of OH products from IR activated MVK-OO, while $k_{\text {fall }}$ is a purely experimental effect coming from the molecules moving out of the UV probe volume. The latter arises from the terminal velocity of the jet and the kinetic energy release to the OH products upon dissociation of hydroperoxide (HPBD). ${ }^{18,23}$ Following IR activation of MVK-OO with two quanta of CH stretch, the OH products appear on a hundreds of nanosecond time scale and fall off on a greater than $1 \mu \mathrm{~s}$ time scale. For the feature at $6200 \mathrm{~cm}^{-1}$, the temporal profile is dominated by the exponential fall off term ( $>95 \%$ ) at long IR-UV time delays ( $\mathrm{t}>1300 \mathrm{~ns}$ ). The relatively large portion of the profile that is dominated by this single term allows for fitting of experimental data without problematic correlation between the two fitting parameters. For the rate measurement at $5975 \mathrm{~cm}^{-1}$, the significantly slower OH appearance rate means that the temporal profile is dominated by the exponential fall off term only at much longer IR-UV time delays ( $\mathrm{t}>2600 \mathrm{~ns}$ ). When this longer-time portion of the curve is fit to a single exponential, a $k_{\text {fall }}$ value is obtained that is within uncertainty of the $k_{\text {fall }}$ value derived from fitting the entire curve. This indicates that the correlation between $k_{\text {rise }}$ and $k_{\text {fall }}$ should not affect the value of $k_{\text {rise }}$. However, the smaller portion of the curve that is dominated by the fall term leads to a greater uncertainty in $k_{\text {fall }}$ and a correspondingly larger uncertainty in $k_{\text {rise }}$. The time delay profiles are measured several times and the resulting curves are averaged together. Reported uncertainties are $\pm 1 \sigma$ from fitting and repeated measurements.

At a fixed IR-UV time delay of 800 ns , the relative intensity of MVK-OO features in the IR action spectrum will depend on their unimolecular decay rates ( $k_{\text {rise }}$ ) or corresponding rise times $\left(1 / k_{\text {rise }}\right.$,
$\tau_{\text {rise }}$ ) to OH products. Using a typical experimental fall rate ( $k_{\text {fall }}$ ) of $0.8 \times 10^{6} \mathrm{~s}^{-1}\left(\tau_{\text {fall }}=1250 \mathrm{~ns}\right.$ ), Eq. S1 reduces to the following expression for relative intensity at $t=800 \mathrm{~ns}$

$$
\begin{equation*}
F\left(t=8 \times 10^{-7} s\right)=A^{\prime}\left(1-\exp \left(-k_{\text {rise }}\left(8 \times 10^{-7} s\right)\right)\right) \tag{S2}
\end{equation*}
$$

This expression is plotted as a function of $k_{\text {rise }}$ and corresponding $\tau_{\text {rise }}$ in Figure S 12 with $A^{\prime}$ set equal to 1 . Vibrationally activated MVK-OO that decays rapidly (< 100 ns ) to OH products will be observed with uniform and highest efficiency. However, vibrationally activated MVK-OO that decays more slowly to OH products will be detected with lower efficiency and may appear to have weaker intensity in the IR action spectrum. For example, the efficiency will decrease by as much as 5 -fold if the unimolecular decay time slows to 3000 ns.

S5. Details of rate calculations
The RRKM calculations using semiclassical transition state theory (SCTST) are performed using the Multiwell suite of programs. ${ }^{26-27}$ The reactant density of states is calculated using the DENSUM program, with standard Whitten-Rabinovitch method, while the cumulative reaction probabilities including tunneling are computed using the SCTST code in Multiwell. RRKM calculations using an asymmetric Eckart model are implemented in the MESS suite of programs. ${ }^{28-29}$

As described in the main text, unimolecular decay of syn-cis-MVK-OO will predominantly occur via the lower energy syn-trans-MVK-OO TS. Vibrationally excited syn-cis-MVK-OO can isomerize to syn-trans-MVK-OO via a low barrier (Figure S7) to internal rotation of the vinyl group. At a given IR excitation energy, the less stable syn-cis conformer ( $1.75 \mathrm{kcal} \mathrm{mol}^{-1}$ ) will reach a higher energy rovibrational state of syn-MVK-OO. As a result, the RRKM calculations for syn-cis-MVK-OO will utilize the same input parameters as syn-trans-MVK-OO, but a given excitation energy will access a higher total energy and result in a more rapid unimolecular decay rate for syn-cis-MVK-OO (Figure S11 and Table S11). As the energies investigated in this study are well above the barrier between the syn-cis
and syn-trans conformers, the density of states in the RRKM calculation corresponds to that of the sum of the two conformers. The inclusion of the vinyl torsional potential accounts for this effect.

The statistical RRKM rate calculations for the electrocyclic ring-closing reaction from anti-MVK-OO to dioxole (11) are performed using the MESS suite of programs. ${ }^{28-29}$ The energy dependent rates and corresponding lifetimes are presented in Figure S13 and Table S11. These calculations are based on the zero-pointed corrected stationary point energies from our high-level electronic structure calculations (see Table S2). The energy of the resulting dioxole product is $-24.3 \mathrm{kcal} \mathrm{mol}^{-1}$. The TS barrier for the electrocyclization reaction is predicted to be $15.1 \mathrm{kcal} \mathrm{mol}^{-1}$ (an effective barrier of 12.5 kcal mol ${ }^{-1}$ for the lower energy anti-trans-MVK-OO conformer). As described below, the methyl and vinyl torsional modes of the reactant and the methyl torsional mode of the TS are treated as onedimensional hindered rotors. Other vibrational modes of anti-MVK-OO and the TS are treated with the rigid-rotor harmonic oscillator approximation, but using anharmonic frequencies. The vibrational frequencies of the reactants and the TS are presented in Tables S7 and S8, respectively. In the RRKM rate calculations, rovibrational parameters of anti-trans-MVK-OO are utilized as the reactant input parameters. As with the two syn conformers of MVK-OO, the two anti conformers are expected to readily interconvert via a low effective barrier of ca. $8 \mathrm{kcal} \mathrm{mol}^{-1}$. Therefore, to calculate the rate of reaction of anti-cis-MVK-OO, the same input parameters are used, but a given excitation energy will access a higher total energy and result in a more rapid unimolecular decay rate for anti-cis-MVK-OO. The effective symmetry numbers are 1 for the anti-MVK-OO with a plane of symmetry and $1 / 2$ for the transition state. For completeness, tunneling is included in the statistical RRKM calculations using the asymmetric Eckart model with an imaginary frequency of $471 \mathrm{~cm}^{-1}$. However, with such a low imaginary frequency, tunneling is unlikely to be important in this reaction. The computed unimolecular decay rates of anti-cis and anti-trans-MVK-OO to dioxole (11) at an excitation energy of $6175 \mathrm{~cm}^{-1}$ are $2.6 \times 10^{8} \mathrm{~s}^{-1}$ and $3.2 \times 10^{-8} \mathrm{~s}^{-1}$, respectively.

For all RRKM calculations, the methyl and vinyl torsional modes are treated as one-dimensional hindered rotors. The relaxed torsional potentials are computed on a grid with $30^{\circ}$ spacings at the $\operatorname{CCSD}(T) / c c-p V T Z-F 12 / / B 2 P L Y P-D 3 / c c-p V T Z$ level of theory. For the methyl torsional mode of syn-trans-MVK-OO, the barrier to internal rotation is $808 \mathrm{~cm}^{-1}$ and the harmonic frequency is $198 \mathrm{~cm}^{-1}$. For the methyl torsional mode of anti-trans-MVK-OO, the barrier to internal rotation is $462 \mathrm{~cm}^{-1}$ and the harmonic frequency is $151 \mathrm{~cm}^{-1}$. For the TS from anti-trans-MVK-OO to dioxole, the methyl torsional mode barrier is $336 \mathrm{~cm}^{-1}$ and the harmonic frequency is $130 \mathrm{~cm}^{-1}$. The methyl torsional potentials are 3 fold symmetric.

For the vinyl torsional potentials of the reactants (syn and anti MVK-OO) the calculated torsion potentials are fit to a 12 -term Fourier series given by

$$
\begin{equation*}
V(x)=V_{0}+\sum_{n=1}^{12} V_{n} \cos (n x) \tag{S3}
\end{equation*}
$$

The TS from syn-trans-MVK-OO to HPBD also contains a vinyl torsional mode. As the TS vinyl torsional mode is not symmetric, it is fit to a Fourier series including sine terms, given by

$$
\begin{equation*}
V(x)=V_{0}+\sum_{n=1}^{6} V_{n}^{c} \cos (n x)+V_{n}^{s} \sin (n x) \tag{S4}
\end{equation*}
$$

The fitting parameters are given in Table S12. Other vibrational modes are treated with the harmonic oscillator approximation, but using anharmonic frequencies, calculated at the B2PLYP-D3/cc-pVTZ level of theory, and given in Table S7 for the reactant and Table S8 for the TS. The low rotational temperature of the Criegee intermediates is modeled with $\mathrm{J}=0$ in both the SCTST and asymmetric Eckart RRKM calculations.

Scheme S1. Synthesis of diiodoalkene precursor (Z/E)-1,3-diiodobut-2-ene from but-2-yn-1-ol following the methods of Refs. 1 (S1A) and 3 (S1B), respectively.

S1A.


S1B.


Scheme S2. Formation of dioxole $(\mathrm{m} / \mathrm{z}=86)$ from reaction of $\mathrm{O}_{2}$ with monoiodoalkene radicals $\left(\mathrm{C}_{4} \mathrm{H}_{6} \mathrm{I}\right)$.


(Z)-1,3-diiodobut-2-ene ( $E$ )-1,3-diiodobut-2-ene


Figure S1. (Upper) $500 \mathrm{MHz}{ }^{1} \mathrm{H}$ NMR and (lower) $125 \mathrm{MHz}{ }^{13} \mathrm{C}\left\{{ }^{1} \mathrm{H}\right\}$ NMR of (Z)-1,3-diiodobut-2-ene (red) and ( $E$ )-1,3-diiodobut-2-ene mixture (blue) in $\mathrm{CDCl}_{3}$. A $\sim 14: 1$ ratio is determined by the normalized integrated intensity of the methine hydrogen of ( $Z$ )-1,3-diiodobut-2-ene ( $\delta 5.7 \mathrm{ppm}, 1 \mathrm{H}, 1.00$ integrated intensity) to the methine hydrogen of ( $E$ )-1,3-diiiodobut-2-ene ( $\delta 6.0 \mathrm{ppm}, 1 \mathrm{H}, 0.07$ integrated intensity).


Figure S2. UV-Vis spectra for (Z/E)-1,3-diiodobut-2-ene (red, $0.07 \mathrm{mmol} / \mathrm{L}$ ) and $\mathrm{CH}_{2} \mathrm{I}_{2}$ (black, 0.19 $\mathrm{mmol} / \mathrm{L}$ ) in hexanes.


Figure S3. FTIR spectrum of (Z/E)-1,3-diiodobut-2-ene on a KBr plate from 400 to $3200 \mathrm{~cm}^{-1}$. A complementary theoretical calculation of vibrational frequencies is given in Ref. 5.


Figure S4. Plot of the distinguished coordinate CASPT2(9e,7o)/CBS//CASPT2/cc-pVDZ minimum energy paths for addition of $\mathrm{O}_{2}$ to either the $\mathrm{C}_{(1)}$ (blue dotted line) or $\mathrm{C}_{(3)}$ sites (solid black line) in $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{I}) \mathrm{CH}_{3}(\operatorname{Int}(\mathbf{1}))$.


Figure S5. Plot of the potential energy for torsional scans of the OOCC group for a C-O bond length of $1.95 \AA$ for addition of $\mathrm{O}_{2}$ to either the $\mathrm{C}_{(1)}$ (blue dotted line) or $\mathrm{C}_{(3)}$ sites (solid black line) of $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{I}) \mathrm{CH}_{3}(\operatorname{Int}(1))$.


Figure S6. (Upper) TOF mass spectrum of (Z/E)-1,3-diiodobut-2-ene precursor sample (heated to $45^{\circ} \mathrm{C}$ ) obtained upon 118 nm VUV photoionization. Mass channels ( $\mathrm{m} / \mathrm{z}=308 \mathrm{C}_{4} \mathrm{H}_{6} \mathrm{I} 2, \mathrm{~m} / \mathrm{z}=181 \mathrm{C}_{4} \mathrm{H}_{6} \mathrm{I}, \mathrm{m} / \mathrm{z}=$ $127 \mathrm{I}, \mathrm{m} / \mathrm{z}=254 \mathrm{I}_{2}$ ) result from photoionization of the precursor. Residual dichloromethane (DCM, m/z $=85$ ) from the synthetic workup is observed. (Lower) TOF mass spectrum of $(Z / E)-1,3$-diiodobut-2-ene precursor sample in a $20 \% \mathrm{O}_{2} / \mathrm{Ar}$ carrier gas with 248 nm photolysis along the quartz capillary tube reactor and 118 nm VUV photoionization. Inset shows the $\mathrm{m} / \mathrm{z}=86$ mass channel (ticks at $0.5 \mathrm{~m} / \mathrm{z}$ ) attributed to the MVK-OO Criegee intermediate.


Figure S7. Isomerization barriers between the four conformers of MVK-OO. The cis/trans isomerization barriers are shown in black, while the syn/anti isomerization barrier is shown in red.


Figure S8. Simulated rotational band contour (cyan) at 10 K for the strongest predicted IR transition of syn-trans-MVK-OO at $6200 \mathrm{~cm}^{-1}$. The overall breadth is approximated by a $\sim 3 \mathrm{~cm}^{-1}$ FWHM Gaussian lineshape (black), which is used to represent the rotational band contour in the computed IR spectra (Figure 4). A simulation at the laser linewidth (gray) is also shown for comparison.


Figure S9. Computed anharmonic IR stick spectra for the dioxole (top, green) and cis and trans HPBD (bottom, grey and purple, respectively) in the $2 v_{\mathrm{CH}}$ region at the B2PLYP-D3/cc-pVTZ level of theory. Note that CH stretch overtone excitation does not provide sufficient energy to initiate unimolecular decay of cis or trans-HPBD, which have barriers to OH production of 19.2 and $21.0 \mathrm{kcal} \mathrm{mol}^{-1}$, respectively. Similarly, dioxole requires $21.8 \mathrm{kcal} \mathrm{mol}^{-1}$ for unimolecular decay, again exceeding the energy provided by two quanta of CH stretch excitation. (See Table S2 for energetics.)


Figure S10. Representative temporal profile of OH products observed by UV laser-induced fluorescence (LIF) following IR excitation of MVK-OO at $6200.4 \mathrm{~cm}^{-1}$. The IR-UV time delay was stepped in 20 ns increments. Experimental data (gray points) is fit to a dual exponential function (Eqn. (S1), black line) to obtain an OH appearance rate of $(2.3 \pm 0.2) \times 10^{6} \mathrm{~s}^{-1}$ and an experimental fall rate of $(0.69 \pm 0.02) \times 10^{6} \mathrm{~s}^{-}$ ${ }^{1}$.


Figure S11. Experimental rates and corresponding lifetimes (semi-log scales) for the unimolecular decay of MVK-OO to OH products (gray points) with $\pm 1 \sigma$ uncertainty from fitting. The statistical RRKM rates are calculated for syn-trans-MVK-OO (cyan) and syn-cis-MVK-OO (purple) using asymmetric Eckart (solid line) and SCTST (dashed line) tunneling models.


Figure S12. Simulated OH signal intensity obtained at a fixed IR-UV time delay of 800 ns as a function of its appearance time ( $\tau_{\text {rise }}$ ) or rate ( $k_{\text {rise }}$ ) as given in Equation S2. For OH appearance times shorter than 100 ns (left dashed vertical black line), OH products will be detected with highest and uniform efficiency. For OH appearance times observed experimentally upon IR activation of MVK-OO (orange and cyan vertical lines), the relative intensities of the corresponding MVK-OO features in the IR action spectrum are only slightly affected. However, for OH appearance times greater than 3000 ns (right dashed vertical black line), the detection efficiency will decrease at least 5-fold and OH products may be difficult to detect under the present experimental conditions.


Figure S13. Statistical RRKM rates and corresponding lifetimes (semi-log scale) for the cyclization reaction from anti-cis-MVK-OO (blue) and anti-trans-MVK-OO (orange) to dioxole.

Table S1. Vertical ionization energies (VIE), adiabatic ionization energies (AIE), and T1 diagnostic (T1) computed at the CCSD(T)-F12/CBS(TZ-F12,QZ-F12)//B2PLYP-D3/cc-pVTZ levels of theory for the four MVK-OO conformers and various other intermediates.

| MVK-OO conformer | VIE $(\mathrm{eV})^{\mathrm{a}}$ | AIE $(\mathrm{eV})^{\mathrm{b}}$ | $\mathrm{T1}^{\mathrm{c}}$ |
| :---: | :---: | :---: | :---: |
| anti-cis | 8.80 | 8.65 | 0.023 |
| anti-trans | 8.65 | 8.54 | 0.022 |
| syn-cis | 8.66 | 8.55 | 0.023 |
| syn-trans | 8.69 | 8.61 | 0.024 |
| Isomers |  |  |  |
| Dioxole (11) | 8.71 | 8.44 | 0.042 |
| HPBD (1b) | 9.02 | 8.67 | 0.023 |
| HB (3) | 10.95 | 9.56 | 0.019 |
| $\beta$-dicarbonyl (13) | 10.06 | 9.64 | 0.029 |
| enol (14) | 9.47 | 9.12 | 0.020 |

[^1]Table S2. ANL0-B2F stationary point energies ( $\mathrm{kcal} \mathrm{mol}^{-1}$ ) on the $\mathrm{C}_{4} \mathrm{H}_{6} \mathrm{O}_{2}$ potential energy surface. ${ }^{\mathrm{a}, \mathrm{b}}$

| Species | Label | $\begin{aligned} & \hline \text { CCSD(T) } \\ & / \text { CBS }^{c} \\ & \hline \end{aligned}$ | $\begin{aligned} & \hline \hline \text { ZPE } \\ & \text { Har. }{ }^{\mathrm{d}} \\ & \hline \hline \end{aligned}$ | $\mathrm{T}(\mathrm{Q})^{\mathrm{e}}$ | CoreVal. ${ }^{f}$ | Rel. ${ }^{\text {g }}$ | $\begin{aligned} & \text { Anh. } \\ & \text { ZPE }^{\text {h }} \end{aligned}$ | Total ${ }^{\text {i }}$ | T1 ${ }^{\text {j }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Minima |  |  |  |  |  |  |  |  |  |
| syn-trans-MVK-OO |  | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0.034 |
| syn-cis-MVK-OO |  | 1.94 | -0.19 | 0.01 | 0.00 | 0.01 | 0.00 | 1.76 | 0.036 |
| anti-trans-MVK-OO |  | 2.75 | -0.10 | -0.07 | 0.02 | 0.00 | -0.03 | 2.57 | 0.034 |
| anti-cis-MVK-OO |  | 2.78 | 0.03 | 0.20 | 0.06 | 0.00 | -0.01 | 3.05 | 0.035 |
| trans-HPBD | 1b | -15.12 | 0.00 | 1.41 | -0.13 | 0.05 | -0.06 | -13.83 | 0.013 |
| cis-HPBD | 1a | -13.14 | -0.17 | 1.41 | -0.12 | 0.04 | -0.06 | -12.02 | 0.013 |
| dioxole | 11 | -27.02 | 1.27 | 1.54 | 0.04 | 0.06 | -0.15 | -24.28 | 0.014 |
| trans-dioxirane | 6a | -16.98 | 0.08 | 1.45 | 0.25 | -0.06 | 0.00 | -15.28 | 0.013 |
| cis-dioxirane | 6b | -18.64 | 0.24 | 1.43 | 0.26 | -0.06 | 0.03 | -16.77 | 0.014 |
| $\beta$-dicarbonyl | 13 | -94.46 | 0.36 | 1.68 | -0.07 | 0.09 | -0.02 | -92.42 | 0.015 |
| enol | 14 | -99.83 | 1.53 | 1.61 | -0.26 | 0.18 | -0.16 | -96.93 | 0.017 |
| HB | 3 | -84.85 | 1.21 | 1.73 | -0.16 | 0.17 | -0.06 | -81.97 | 0.014 |
| trans-OBD + OH | $2 \mathrm{~b}+\mathrm{OH}$ | 10.62 | -5.06 | 1.61 | 0.01 | -0.03 | 0.11 | 7.16 ${ }^{\text {k }}$ | 0.020 |
|  |  |  |  |  |  |  |  |  | 0.008 |
| cis-OBD + OH | $2 \mathrm{a}+\mathrm{OH}$ | 11.22 | -5.16 | 1.62 | 0.02 | -0.03 | 0.18 | 7.75 ${ }^{\text {k }}$ | 0.019 |
|  |  |  |  |  |  |  |  |  | 0.008 |
| AHP | 7 | 0.5 | -0.8 | - | - | - | - | $1.3{ }^{1}$ | 0.013 |
| $\mathrm{OA}+\mathrm{OH}$ | $8+\mathrm{OH}$ | 23.6 | -6.2 | - | - | - | - | $18.8{ }^{\text {k, } 1}$ | 0.021 |
| Transition States |  |  |  |  |  |  |  |  |  |
| syn-cis to syn-trans |  | 8.17 | -0.63 | 0.45 | 0.01 | -0.01 | -0.03 | 7.97 | 0.031 |
| MVK-OO |  |  |  |  |  |  |  |  |  |
| anti-cis to anti-trans |  | 11.56 | -0.71 | 0.41 | 0.01 | 0.00 | -0.03 | 11.24 | 0.031 |
| MVK-OO |  |  |  |  |  |  |  |  |  |
| syn-trans-MVK-OO to |  | 19.66 | -2.52 | 0.78 | 0.07 | -0.02 | -0.01 | 17.96 | 0.025 |
| cis-HPBD |  |  |  |  |  |  |  |  |  |
| syn-cis-MVK-OO to |  | 20.93 | -2.58 | 0.81 | 0.05 | -0.02 | 0.00 | 19.19 | 0.026 |
| trans-HPBD |  |  |  |  |  |  |  |  |  |
| anti-trans-MVK-OO to |  | 26.94 | -3.12 | 0.67 | 0.15 | -0.03 | -0.01 | 24.57 | 0.025 |
| AHP |  |  |  |  |  |  |  |  |  |
| anti-cis-MVK-OO to |  | 14.64 | -0.27 | 0.52 | 0.25 | -0.02 | -0.04 | 15.06 | 0.032 |
| dioxole |  |  |  |  |  |  |  |  |  |
| anti-cis-MVK-OO to |  | 26.29 | -1.19 | 0.07 | 0.32 | -0.07 | -0.02 | 25.38 | 0.039 |
| cis-dioxirane |  |  |  |  |  |  |  |  |  |
| cis-dioxirane to syn-cis- |  | 22.11 | -0.79 | -0.18 | 0.30 | -0.07 | -0.01 | 21.35 | 0.038 |
| MVK-OO |  |  |  |  |  |  |  |  |  |
| anti-trans-MVK-OO to |  | 21.04 | -0.96 | -0.31 | 0.29 | -0.08 | -0.03 | 19.93 | 0.038 |
| trans-dioxirane |  |  |  |  |  |  |  |  |  |
| trans-dioxirane to syn- |  | 23.26 | -0.76 | -0.27 | 0.32 | -0.07 | -0.02 | 22.44 | 0.038 |
|  |  |  |  |  |  |  |  |  |  |
| cis-dioxirane to transdioxirane |  | -14.76 | -0.18 | 1.46 | 0.25 | -0.06 | -0.01 | -13.32 | 0.013 |
| $\beta$-dicarbonyl to enol |  | -36.0 | -2.9 | $-1$ | - ${ }^{1}$ | _1 | $-1$ | $-37.4^{1}$ | 0.018 |

${ }^{2}$ All energies are evaluated relative to the ground (syn-trans) MVK-OO configuration.
${ }^{\mathrm{b}}$ All species are defined in Table S13.
${ }^{\text {c }}$ CCSD(T)-F12b/CBS(TZ-F12,QZ-F12)//B2PLYP-D3/cc-pVTZ energy.
${ }^{\text {d }}$ B2PLYP-D3/cc-pVTZ harmonic zero-point energy correction.
${ }^{e} \operatorname{CCSDT}(\mathrm{Q}) /$ cc-pVDZ correction.
${ }^{\mathrm{f}}$ Core valence correction evaluated from CCSD(T)/CBS(cc-pcVTZ,cc-pcVQZ) calulations.
${ }^{\text {g }}$ Douglas-Kroll relativistic correction from CCSD(T)/aug-cc-pcvtz-DK calculations.
${ }^{\text {h }}$ B2PLYP-D3/cc-pVTZ anharmonicity correction to the harmonic zero-point energy.
${ }^{\mathrm{i}}$ ANL0-B2F energy evaluated as the sum of the other energies.
${ }^{\mathrm{j}}$ T1 diagnostic.
${ }^{\mathrm{k}}$ The OH energy includes an additional -0.11 lowering to account for the spin-orbit lowering.
${ }^{1}$ Higher order corrections were not evaluated. Instead, we report CCSD(T)-F12b/CBS(TZ-F12,QZ-F12)//B2PLYP-D3/cc-pVTZ predictions. For these species, we still account for the significant multireference effects in the reference MVK-OO, by appending a constant correction of $1.5 \mathrm{kcal} \mathrm{mol}^{-1}$.

Table S3. Stationary point energies ( $\mathrm{kcal} \mathrm{mol}^{-1}$ ) of relevance to OO bond fission of trans-HPBD (1b).

| Species | State | PT2 ${ }^{\text {a }}$ | $\begin{aligned} & \text { MRCI- } \\ & \text { SD+Q }{ }^{\text {b }} \end{aligned}$ | $\operatorname{CCSD}(\mathrm{T})^{\mathrm{c}}$ | ZPE ${ }^{\text {d }}$ | Total ${ }^{\text {e }}$ (Rel. to Prod.) | Total ${ }^{\mathrm{f}}$ (Rel. to syn-trans) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| trans-HPBD to RC(1) | ${ }^{1} \mathrm{~A}$ | -4.23 | -3.21 |  | 1.10 | -3.13 | 4.03 |
| $\mathrm{RC}(1)$ | ${ }^{1} \mathrm{~A}^{\prime}$ | -6.74 | -6.21 |  | 1.93 | -4.81 | 2.35 |
|  | ${ }^{1} \mathrm{~A}$ " | -6.30 | -5.80 |  |  |  |  |
|  | ${ }^{3} \mathrm{~A}^{\prime}$ | -6.63 | -6.12 | -6.72 |  |  |  |
|  | ${ }^{3} \mathrm{~A}$ " | -6.30 | -5.79 |  |  |  |  |
| $\mathrm{RC}(1)$ to $\mathrm{RC}(2)$ | ${ }^{1} \mathrm{~A}^{\prime}$ | -5.83 | -5.51 |  |  |  |  |
|  | ${ }^{1} \mathrm{~A}$ " | -5.81 | -5.50 |  |  |  |  |
|  | ${ }^{3} \mathrm{~A}^{\prime}$ | -5.77 | -5.45 | -5.78 |  |  |  |
|  | ${ }^{3} \mathrm{~A}$ " | -5.81 | -5.49 |  | 1.44 | -4.37 | 2.79 |
| $\mathrm{RC}(2)$ | ${ }^{1} \mathrm{~A}^{\prime}$ | -7.15 | -6.54 |  | 1.82 | -5.33 | 1.83 |
|  | ${ }^{1} \mathrm{~A}$ " | -6.57 | -6.03 |  |  |  |  |
|  | ${ }^{3} \mathrm{~A}^{\prime}$ | -7.14 | -6.52 | -7.26 |  |  |  |
|  | ${ }^{3} \mathrm{~A}^{\prime \prime}$ | -6.61 | -6.01 |  |  |  |  |
| $\mathrm{RC}(2)$ to HB | ${ }^{1} \mathrm{~A}$ | -6.60 | -5.79 |  | 1.81 | -4.79 | 2.37 |

${ }^{\text {a }}$ CASPT2(6e,6o)/CBS(TZ,QZ)//CASPT2(6e,6o)/cc-pVTZ electronic energies relative to the ground state energy of $\mathrm{OH}+\mathrm{OBD}(2 \mathrm{~b})$; i.e., relative to the trans-configuration of OBD.
${ }^{\mathrm{b}}$ MRCISD+Q(6e,6o)/CBS(TZ,QZ)//CASPT2(6e,6o)/cc-pVTZ electronic energies relative to the ground state energy of $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{O}) \mathrm{CH}_{2}+\mathrm{OH}$.
${ }^{\text {c }}$ CCSD (T)-F12/CBS(TZ-F12,QZ-F12)//CASPT2(6e,6o)/cc-pVTZ electronic energies relative to the ground state energy of $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{O}) \mathrm{CH}_{2}+\mathrm{OH}$.
${ }^{\mathrm{d}}$ CASPT2 $(6 \mathrm{e}, 6 \mathrm{o}) /$ cc-pVTZ zero-point energies relative to the zero-point energy of $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{O}) \mathrm{CH}_{2}+$ OH. Number in italics is from B2PLYP-D3/cc-pVTZ calculations.
${ }^{e}$ Sum of CASPT2(6e,6o)/CBS electronic energy and CASPT2(6e,6o)/cc-pVTZ zero-point energy relative to the corresponding energy for $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{O}) \mathrm{CH}_{2}+\mathrm{OH}$.
${ }^{\mathrm{f}}$ Total energy as in e, but with the energy now referenced to the energy of the ground state of MVK-OO through the ANL0-B2F energy for $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{O}) \mathrm{CH}_{2}+\mathrm{OH}$.

Table S4. Stationary point energies ( $\mathrm{kcal} \mathrm{mol}^{-1}$ ) for torsional rotations about the CO bond in syn- and anti-MVK-OO.

| Species | PT2 $^{\mathrm{a}}$ <br> Splitting | MRCISD+Q <br> Splitting | Triplet $^{\mathrm{c}}$ <br> Energy | ZPE $^{\mathrm{d}}$ | Total $^{\mathrm{e}}$ |
| :--- | :--- | :--- | :--- | :--- | :--- |
| syn-cis to anti-cis MVK-OO | 1.05 | 0.93 | 29.25 | -1.16 | 30.63 |
| syn-trans to anti-trans MVK-OO | 1.25 | 1.10 | 29.45 | -1.27 | 30.93 |

${ }^{2}$ Splitting between the singlet and triplet states at the singlet torsional saddle point calculated at the PT2(4e,4o)/CBS(TZ,QZ)//PT2(4e,4o)/cc-pVTZ level.
${ }^{\mathrm{b}}$ Splitting between the singlet and triplet states at the singlet torsional saddle point calculated at the MRCISD+Q(4e,4o)/CBS(TZ,QZ)//PT2(4e,4o)/cc-pVTZ level.
${ }^{c} \operatorname{CCSD}(\mathrm{~T})-\mathrm{F} 12 \mathrm{~b} / \mathrm{cc}-\mathrm{pVTZ}-\mathrm{F} 12$ energy for the triplet state relative to syn-trans-MVK-OO. The triplet state energy is calculated at the $\mathrm{PT} 2(4 \mathrm{e}, 4 \mathrm{o})$ /cc-pVTZ geometry.
${ }^{\text {d }}$ Zero-point energy (ZPE) for the singlet torsional saddle point calculated at the PT2(4e,4o)/cc-pVTZ level relative to the B2PLYP-D3/cc-pVTZ ZPE for syn-trans-MVK-OO.
${ }^{\text {e }}$ Zero-point corrected energy of the singlet torsional saddle point relative to syn-trans-MVK-OO from the PT2(4e,4o) singlet-triplet splitting, the CCSD(T)-F12b triplet energy, and a presumed $1.5 \mathrm{kcal} \mathrm{mol}^{-1}$ CCSDT(Q)/cc-pVDZ correction.

Table S5. Stationary point energies ( $\mathrm{kcal} \mathrm{mol}^{-1}$ ) of relevance to OO bond fission in dioxole (11).

| Species | PT2 ${ }^{\text {a }}$ <br> Splitting | $\text { MRCISD+Q }{ }^{\text {b }}$ <br> Splitting | Reference ${ }^{\text {c }}$ Energy | ZPE ${ }^{\text {d }}$ | Total ${ }^{\text {e }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| dioxole to diradical | -4.8 | -3.6 | 1.3 | -0.5 | -2.5 |
| diradical | -6.9 | -6.2 | -10.8 | -2.4 | -18.1 |
| diradical to $\beta$-dicarbonyl | -7.0 | -5.9 | -10.8 | -2.5 | -18.7 |

${ }^{\text {a }}$ Splitting (between the singlet for the given species and the triplet reference configuration) calculated at the PT2(4e,4o)/CBS(TZ,QZ)//PT2(4e,4o)/cc-pVTZ level.
${ }^{\mathrm{b}}$ Splitting (between the singlet for the given species and the triplet reference configuration) calculated at the MRCISD+Q(4e,4o)/CBS(TZ,QZ)/PT2(4e,4o)/cc-pVTZ level.
${ }^{c}$ CCSD(T)-F12b/cc-pVTZ-F12 energy for the reference state relative to syn-trans-MVK-OO. The reference state is taken to be the triplet state at the corresponding nearby singlet geometry.
${ }^{\text {d }}$ Zero-point energy (ZPE) calculated at the PT2(4e,4o)/cc-pVTZ level relative to the B2PLYP-D3/ccpVTZ ZPE for syn-trans-MVK-OO.
${ }^{\text {e }}$ Zero-point corrected energy relative to syn-trans-MVK-OO from the PT2(4e,4o) splitting, the $\operatorname{CCSD}(\mathrm{T})$-F12b triplet energy, and a presumed $\operatorname{CCSDT}(\mathrm{Q}) / \mathrm{cc}-\mathrm{pVDZ}$ correction of $1.5 \mathrm{kcal} \mathrm{mol}^{-1}$.

Table S6. Strongest IR transitions predicted with second order vibrational perturbation theory (VPT2) at the B2PLYP-D3/cc-pVTZ level of theory for syn-trans, syn-cis, anti-trans, and anti-cis MVK-OO from 5700 to $6300 \mathrm{~cm}^{-1}$ with assignments, energies, and intensities.

| Assignment | Wavenumber ( $\mathrm{cm}^{-1}$ ) | IR intensity ( $\mathrm{km} \mathrm{mol}^{-1}$ ) |
| :---: | :---: | :---: |
| syn-trans-MVK-OO |  |  |
| $2 v_{1}$ | 6200.0 | 1.44 |
| $\nu_{2}+v_{3}$ | 6100.1 | 0.17 |
| $v_{1}+v_{4}$ | 6087.9 | 0.26 |
| $v_{2}+v_{4}$ | 6087.7 | 0.17 |
| $v_{3}+v_{4}$ | 6063.1 | 0.15 |
| $2 v_{4}$ | 6057.0 | 0.26 |
| $2 v_{3}$ | 6039.5 | 0.13 |
| $2 v_{2}$ | 6027.4 | 0.32 |
| $v_{3}+v_{21}$ | 5992.7 | 0.11 |
| $2 v_{21}$ | 5833.4 | 0.32 |
| $v_{5}+v_{21}$ | 5782.7 | 0.21 |
| syn-cis-MVK-OO |  |  |
| $2 v_{1}$ | 6210.4 | 1.14 |
| $v_{2}+v_{3}$ | 6108.7 | 0.12 |
| $\nu_{1}+v_{3}$ | 6080.0 | 0.39 |
| $2 v_{3}$ | 6044.8 | 0.31 |
| $2 v_{2}$ | 6038.4 | 0.36 |
| $2 v_{4}$ | 5984.1 | 0.30 |
| $v_{4}+v_{21}$ | 5961.8 | 0.15 |
| $2 v_{21}$ | 5822.3 | 0.29 |
| $v_{5}+v_{21}$ | 5773.9 | 0.20 |
| anti-trans-MVK-OO |  |  |
| $2 v_{1}$ | 6185.8 | 1.06 |
| $v_{1}+v_{2}$ | 6181.8 | 0.39 |
| $v_{2}+v_{3}$ | 6109.2 | 0.13 |
| $2 v_{2}$ | 6069.8 | 0.39 |
| $v_{1}+v_{3}$ | 6056.5 | 0.24 |
| $2 \nu_{3}$ | 6013.7 | 0.26 |
| $v_{4}+v_{21}$ | 5975.5 | 0.14 |
| $2 v_{4}$ | 5956.9 | 0.38 |
| $2 V_{21}$ | 5877.9 | 0.77 |
| $2 \nu_{5}$ | 5848.4 | 0.10 |
| $v_{5}+v_{21}$ | 5816.3 | 0.22 |
| anti-cis-MVK-OO |  |  |
| $2 v_{1}$ | 6242.9 | 0.46 |
| $\nu_{1}+\nu_{3}$ | 6158.2 | 0.13 |
| $2 v_{2}$ | 6039.9 | 0.18 |
| $v_{3}+v_{4}$ | 6031.7 | 0.43 |
| $2 v_{3}$ | 6030.3 | 0.50 |
| $\nu_{2}+v_{3}$ | 6014.7 | 0.26 |
| $2 \nu_{4}$ | 5988.3 | 0.20 |
| $v_{4}+v_{21}$ | 5981.6 | 0.12 |
| $v_{4}+v_{5}$ | 5934.1 | 0.11 |
| $2 V_{21}$ | 5871.3 | 0.94 |


| $2 v_{5}$ | 5837.8 | 0.13 |
| :---: | :---: | :---: |
| $v_{5}+v_{21}$ | 5806.1 | 0.22 |

Table S7. Fundamental harmonic and anharmonic vibrational frequencies and descriptions computed for syn-trans, syn-cis, anti-trans, and anti-cis MVK-OO in $\mathrm{C}_{\text {s }}$ symmetry at the B2PLYP-D3/cc-pVTZ level of theory.

| Mode | Symmetry | Harmonic <br> Frequency $\left(\mathrm{cm}^{-1}\right)$ | $\begin{gathered} \hline \hline \text { Anharmonic } \\ \text { Frequency } \\ \left(\mathrm{cm}^{-1}\right) \\ \hline \hline \end{gathered}$ | Description |
| :---: | :---: | :---: | :---: | :---: |
| syn-cis-MVK-OO |  |  |  |  |
| $v_{1}$ | $A^{\prime}$ | 3272.8 | 3135.0 | Vinyl out-of-phase CH stretch |
| $v_{2}$ | A' | 3200.0 | 3070.5 | Methine $\mathrm{C}_{(6)} \mathrm{H}_{(7)}$ stretch |
| $v_{3}$ | A' | 3171.7 | 3033.3 | Methyl $\mathrm{C}_{(1)} \mathrm{H}_{(4)}$ stretch |
| $v_{4}$ | A' | 3177.7 | 3022.9 | Vinyl in-phase CH stretch |
| $\nu_{5}$ | $A^{\prime}$ | 3044.5 | 2930.1 | Methyl in-phase CH stretch |
| $v_{6}$ | $A^{\prime}$ | 1669.3 | 1633.8 | Alkene $\mathrm{C}_{(6)} \mathrm{C}_{(8)}$ stretch |
| $v_{7}$ | $\mathrm{A}^{\prime}$ | 1500.5 | 1459.3 | Methyl symmetric CH scissor |
| $\nu_{8}$ | $\mathrm{A}^{\prime}$ | 1474.9 | 1437.4 | Vinyl symmetric CH scissor |
| $\mathrm{v}_{9}$ | $\mathrm{A}^{\prime}$ | 1418.9 | 1383.3 | Methyl umbrella |
| $v_{10}$ | $A^{\prime}$ | 1397.2 | 1360.4 | $\mathrm{C}_{(5)} \mathrm{O}_{(11)}$ stretch |
| $v_{11}$ | $A^{\prime}$ | 1340.7 | 1325.3 | Methine in-plane $\mathrm{C}_{(6)} \mathrm{H}_{(7)}$ wag |
| $v_{12}$ | $A^{\prime}$ | 1286.4 | 1260.4 | $\mathrm{C}_{(5)} \mathrm{C}_{(6)}$ stretch |
| $v_{13}$ | $A^{\prime}$ | 1108.1 | 1081.1 | Vinyl in-plane $\mathrm{C}_{(8)} \mathrm{H}_{(9)} \mathrm{H}_{(10)}$ wag |
| $v_{14}$ | $A^{\prime}$ | 1041.0 | 1019.2 | Methyl rock |
| $v_{15}$ | $A^{\prime}$ | 992.1 | 974.3 | $\mathrm{O}_{(11)} \mathrm{O}_{(12)}$ stretch |
| $v_{16}$ | $A^{\prime}$ | 815.9 | 804.3 | $\mathrm{C}_{(1)} \mathrm{C}_{(5)}$ stretch |
| $v_{17}$ | $\mathrm{A}^{\prime}$ | 623.3 | 617.7 | $\mathrm{C}_{(5)} \mathrm{O}_{(11)} \mathrm{O}_{(12)}$ in-plane bend |
| $v_{18}$ | $\mathrm{A}^{\prime}$ | 485.9 | 483.3 | $\mathrm{C}_{(5)} \mathrm{C}_{(6)} \mathrm{C}_{(8)}$ in-plane bend |
| $v_{19}$ | $A^{\prime}$ | 328.0 | 317.1 | $\mathrm{C}_{(1)} \mathrm{C}_{(5)} \mathrm{O}_{(11)} \mathrm{O}_{(12)}$ ring closing |
| $v_{20}$ | $\mathrm{A}^{\prime}$ | 228.9 | 226.8 | $\mathrm{C}_{(8)} \mathrm{C}_{(6)} \mathrm{C}_{(5)} \mathrm{O}_{(11)}$ ring closing |
| $v_{21}$ | $A^{\prime \prime}$ | 3088.3 | 2943.1 | Methyl out-of-phase CH stretch |
| $v_{22}$ | $A^{\prime \prime}$ | 1451.5 | 1409.1 | Methyl out-of-plane CH wag |
| $v_{23}$ | A" | 1044.5 | 1022.5 | Methyl asymmetric scissor |
| $v_{24}$ | A" | 1024.3 | 1002.3 | Methine out-of-plane $\mathrm{C}_{(6)} \mathrm{H}_{(7)}$ wag |
| $\mathrm{v}_{25}$ | A" | 971.2 | 956.2 | Vinyl out-of-plane $\mathrm{C}_{(8)} \mathrm{H}_{(9)} \mathrm{H}_{(10)}$ wag |
| $v_{26}$ | A" | 665.9 | 653.9 | $\mathrm{C}_{(5)} \mathrm{C}_{(6)} \mathrm{C}_{(8)}$ out-of-plane bend |
| $v_{27}$ | A" | 443.1 | 441.4 | $\mathrm{C}_{(1)} \mathrm{C}_{(5)} \mathrm{O}_{(11)} \mathrm{O}_{(12)}$ out-of-plane ring distortion |
| $v_{28}$ | A" | 275.3 | 264.5 | $\mathrm{C}_{(8)} \mathrm{C}_{(6)} \mathrm{C}_{(5)} \mathrm{O}_{(11)}$ out-of-plane ring distortion |
| $\mathrm{v}_{29}$ | A" | 206.6 | 194.9 | Methyl torsion |
| $v_{30}$ | A" | 66.8 | 65.1 | Vinyl torsion |
| syn-trans-MVK-OO |  |  |  |  |
| $v_{1}$ | $\mathrm{A}^{\prime}$ | 3270.2 | 3130.1 | Vinyl out-of-phase CH stretch |
| $v_{2}$ | $\mathrm{A}^{\prime}$ | 3194.4 | 3060.3 | Methine $\mathrm{C}_{(6)} \mathrm{H}_{(7)}$ stretch |
| $v_{3}$ | $\mathrm{A}^{\prime}$ | 3186.9 | 3054.2 | Methyl $\mathrm{C}_{(1)} \mathrm{H}_{(4)}$ stretch |
| $v_{4}$ | $\mathrm{A}^{\prime}$ | 3178.6 | 3066.9 | Vinyl in-phase CH stretch |
| $v_{5}$ | $A^{\prime}$ | 3052.7 | 2936.0 | Methyl in-phase CH stretch |


| $v_{6}$ | $\mathrm{A}^{\prime}$ | 1661.9 | 1622.8 | Alkene $\mathrm{C}_{(6)} \mathrm{C}_{(8)}$ stretch |
| :---: | :---: | :---: | :---: | :---: |
| $v_{7}$ | $\mathrm{A}^{\prime}$ | 1504.9 | 1462.7 | Methyl symmetric CH scissor |
| $\nu_{8}$ | $\mathrm{A}^{\prime}$ | 1472.9 | 1433.1 | Vinyl symmetric CH scissor |
| $v_{9}$ | $\mathrm{A}^{\prime}$ | 1449.8 | 1405.5 | $\mathrm{C}_{(5)} \mathrm{O}_{(11)}$ stretch |
| $v_{10}$ | $\mathrm{A}^{\prime}$ | 1400.1 | 1364.1 | Methyl umbrella |
| $v_{11}$ | $\mathrm{A}^{\prime}$ | 1337.7 | 1315.1 | $\mathrm{C}_{(5)} \mathrm{C}_{(6)}$ stretch |
| $v_{12}$ | $\mathrm{A}^{\prime}$ | 1292.3 | 1260.4 | Methine in-plane $\mathrm{C}_{(6)} \mathrm{H}_{(7)}$ wag |
| $v_{13}$ | $\mathrm{A}^{\prime}$ | 1076.3 | 1050.9 | Methyl rock |
| $v_{14}$ | $\mathrm{A}^{\prime}$ | 1041.6 | 1024.1 | Vinyl in-plane $\mathrm{C}_{(8)} \mathrm{H}_{(9)} \mathrm{H}_{(10)}$ wag |
| $v_{15}$ | $\mathrm{A}^{\prime}$ | 998.3 | 978.2 | $\mathrm{O}_{(11)} \mathrm{O}_{(12)}$ stretch |
| $v_{16}$ | $\mathrm{A}^{\prime}$ | 814.7 | 802.4 | $\mathrm{C}_{(1)} \mathrm{C}_{(5)}$ stretch |
| $v_{17}$ | $\mathrm{A}^{\prime}$ | 609.9 | 604.4 | $\mathrm{C}_{(5)} \mathrm{O}_{(11)} \mathrm{O}_{(12)}$ in-plane bend |
| $v_{18}$ | $\mathrm{A}^{\prime}$ | 496.9 | 493.1 | $\mathrm{C}_{(5)} \mathrm{C}_{(6)} \mathrm{C}_{(8)}$ in-plane bend |
| $v_{19}$ | $\mathrm{A}^{\prime}$ | 331.9 | 325.9 | $\mathrm{C}_{(1)} \mathrm{C}_{(5)} \mathrm{O}_{(11)} \mathrm{O}_{(12)}$ ring closing |
| $v_{20}$ | $\mathrm{A}^{\prime}$ | 256.0 | 256.8 | $\mathrm{C}_{(8)} \mathrm{C}_{(6)} \mathrm{C}_{(5)} \mathrm{O}_{(11)}$ ring closing |
| $v_{21}$ | A" | 3097.6 | 2948.7 | Methyl out-of-phase CH stretch |
| $v_{22}$ | A" | 1452.9 | 1405.8 | Methyl out-of-plane CH wag |
| $v_{23}$ | A" | 1047.8 | 1021.3 | Methyl asymmetric scissor |
| $v_{24}$ | A" | 1026.8 | 1003.7 | Methine out-of-plane $\mathrm{C}_{(6)} \mathrm{H}_{(7)}$ wag |
| $v_{25}$ | A" | 951.0 | 932.7 | Vinyl out-of-plane $\mathrm{C}_{(8)} \mathrm{H}_{(9)} \mathrm{H}_{(10)}$ wag |
| $v_{26}$ | A" | 682.5 | 671.1 | $\mathrm{C}_{(5)} \mathrm{C}_{(6)} \mathrm{C}_{(8)}$ out-of-plane bend |
| $v_{27}$ | A" | 459.5 | 454.0 | $\mathrm{C}_{(1)} \mathrm{C}_{(5)} \mathrm{O}_{(11)} \mathrm{O}_{(12)}$ out-of-plane ring distortion |
| $v_{28}$ | A" | 283.3 | 280.1 | $\mathrm{C}_{(8)} \mathrm{C}_{(6)} \mathrm{C}_{(5)} \mathrm{O}_{(11)}$ out-of-plane ring distortion |
| $v_{29}$ | A" | 198.1 | 183.8 | Methyl torsion |
| $v_{30}$ | A" | 120.0 | 122.6 | Vinyl torsion |
| anti-cis-MVK-OO |  |  |  |  |
| $v_{1}$ | $\mathrm{A}^{\prime}$ | 3314.0 | 3161.8 | Vinyl out-of-phase CH stretch |
| $v_{2}$ | $\mathrm{A}^{\prime}$ | 3166.8 | 3063.5 | Vinyl in-phase CH stretch |
| $v_{3}$ | $\mathrm{A}^{\prime}$ | 3181.4 | 3041.5 | Methine $\mathrm{C}_{(6)} \mathrm{H}_{(7)}$ stretch |
| $v_{4}$ | $\mathrm{A}^{\prime}$ | 3164.6 | 3028.2 | Methyl $\mathrm{C}_{(1)} \mathrm{H}_{(4)}$ stretch |
| $v_{5}$ | $\mathrm{A}^{\prime}$ | 3054.3 | 2953.3 | Methyl in-phase CH stretch |
| $v_{6}$ | $\mathrm{A}^{\prime}$ | 1640.9 | 1590.4 | Alkene $\mathrm{C}_{(6)} \mathrm{C}_{(8)}$ stretch |
| $v_{7}$ | $\mathrm{A}^{\prime}$ | 1508.0 | 1459.1 | Methyl symmetric CH scissor |
| $\nu_{8}$ | $\mathrm{A}^{\prime}$ | 1464.1 | 1428.9 | Vinyl symmetric CH scissor |
| $v_{9}$ | $\mathrm{A}^{\prime}$ | 1437.4 | 1394.7 | $\mathrm{C}_{(5)} \mathrm{O}_{(11)}$ stretch |
| $v_{10}$ | $\mathrm{A}^{\prime}$ | 1418.9 | 1381.0 | Methyl umbrella |
| $v_{11}$ | $\mathrm{A}^{\prime}$ | 1340.3 | 1305.6 | Methine in-plane $\mathrm{C}_{(6)} \mathrm{H}_{(7)}$ wag |
| $v_{12}$ | $\mathrm{A}^{\prime}$ | 1269.9 | 1233.6 | $\mathrm{C}_{(1)} \mathrm{C}_{(5)}$ stretch |
| $v_{13}$ | $\mathrm{A}^{\prime}$ | 1099.4 | 1082.5 | Vinyl in-plane $\mathrm{C}_{(8)} \mathrm{H}_{(9)} \mathrm{H}_{(10)}$ wag |
| $v_{14}$ | $\mathrm{A}^{\prime}$ | 1055.9 | 1028.7 | $\mathrm{O}_{(11)} \mathrm{O}_{(12)}$ stretch |
| $v_{15}$ | $\mathrm{A}^{\prime}$ | 991.0 | 966.1 | Methyl rock |
| $v_{16}$ | $\mathrm{A}^{\prime}$ | 823.8 | 811.1 | $\mathrm{C}_{(5)} \mathrm{C}_{(6)}$ stretch |
| $v_{17}$ | $A^{\prime}$ | 640.4 | 629.0 | $\mathrm{C}_{(5)} \mathrm{O}_{(11)} \mathrm{O}_{(12)}$ in-plane bend |


| $v_{18}$ | $A^{\prime}$ | 411.3 | 405.0 | $\mathrm{C}_{(5)} \mathrm{C}_{(6)} \mathrm{C}_{(8)}$ in-plane bend |
| :---: | :---: | :---: | :---: | :---: |
| $v_{19}$ | $\mathrm{A}^{\prime}$ | 339.0 | 336.7 | $\mathrm{C}_{(1)} \mathrm{C}_{(5)} \mathrm{O}_{(11)} \mathrm{O}_{(12)}$ in-plane bend |
| $v_{20}$ | $\mathrm{A}^{\prime}$ | 305.4 | 298.5 | $\mathrm{C}_{(8)} \mathrm{C}_{(6)} \mathrm{C}_{(5)} \mathrm{O}_{(11)}$ ring closing |
| $v_{21}$ | A" | 3110.6 | 2967.5 | Methyl out-of-phase CH stretch |
| $v_{22}$ | A" | 1487.1 | 1442.5 | Methyl out-of-plane CH wag |
| $v_{23}$ | $A^{\prime \prime}$ | 1053.4 | 1022.5 | Methyl asymmetric scissor |
| $\mathrm{v}_{24}$ | A" | 1029.3 | 1004.7 | Methine out-of-plane $\mathrm{C}_{(6)} \mathrm{H}_{(7)}$ wag |
| $v_{25}$ | A" | 1004.8 | 984.8 | Vinyl out-of-plane $\mathrm{C}_{(8)} \mathrm{H}_{(9)} \mathrm{H}_{(10)}$ wag |
| $\mathrm{v}_{26}$ | A" | 717.7 | 706.4 | $\mathrm{C}_{(5)} \mathrm{C}_{(6)} \mathrm{C}_{(8)}$ out-of-plane bend |
| $v_{27}$ | A" | 368.3 | 361.0 | $\mathrm{C}_{(8)} \mathrm{C}_{(6)} \mathrm{C}_{(5)} \mathrm{O}_{(11)}$ out-of-plane ring distortion |
| $v_{28}$ | A" | 284.7 | 274.4 | $\mathrm{C}_{(1)} \mathrm{C}_{(5)} \mathrm{O}_{(11)} \mathrm{O}_{(12)}$ out-of-plane bend |
| $v_{29}$ | A" | 165.6 | 165.4 | Vinyl torsion |
| $v_{30}$ | $\mathrm{A}^{\prime \prime}$ | 118.0 | 112.0 | Methyl torsion |
| anti-trans-MVK-OO |  |  |  |  |
| $v_{1}$ | $\mathrm{A}^{\prime}$ | 3261.4 | 3120.7 | Vinyl out-of-phase CH stretch |
| $v_{2}$ | $\mathrm{A}^{\prime}$ | 3227.4 | 3083.8 | Vinyl in-phase CH stretch |
| $v_{3}$ | $\mathrm{A}^{\prime}$ | 3162.0 | 3021.6 | Methine $\mathrm{C}_{(6)} \mathrm{H}_{(7)}$ stretch |
| $v_{4}$ | $\mathrm{A}^{\prime}$ | 3170.4 | 3012.1 | Methyl $\mathrm{C}_{(1)} \mathrm{H}_{(4)}$ stretch |
| $v_{5}$ | $\mathrm{A}^{\prime}$ | 3054.6 | 2965.9 | Methyl in-phase CH stretch |
| $v_{6}$ | $\mathrm{A}^{\prime}$ | 1657.7 | 1619.2 | Alkene $\mathrm{C}_{(6)} \mathrm{C}_{(8)}$ stretch |
| $v_{7}$ | $\mathrm{A}^{\prime}$ | 1512.4 | 1473.0 | Methyl symmetric CH scissor |
| $\nu_{8}$ | $\mathrm{A}^{\prime}$ | 1469.3 | 1436.5 | Vinyl symmetric CH scissor |
| $v_{9}$ | $\mathrm{A}^{\prime}$ | 1436.3 | 1394.5 | $\mathrm{C}_{(5)} \mathrm{O}_{(11)}$ stretch |
| $v_{10}$ | $\mathrm{A}^{\prime}$ | 1390.8 | 1352.2 | Methyl umbrella |
| $v_{11}$ | $\mathrm{A}^{\prime}$ | 1373.3 | 1343.8 | Methine in-plane $\mathrm{C}_{(6)} \mathrm{H}_{(7)}$ wag |
| $v_{12}$ | $\mathrm{A}^{\prime}$ | 1281.4 | 1249.0 | $\mathrm{C}_{(1)} \mathrm{C}_{(5)}$ stretch |
| $v_{13}$ | $\mathrm{A}^{\prime}$ | 1064.9 | 1039.7 | Vinyl in-plane $\mathrm{C}_{(8)} \mathrm{H}_{(9)} \mathrm{H}_{(10)}$ wag |
| $v_{14}$ | $\mathrm{A}^{\prime}$ | 1021.4 | 995.9 | $\mathrm{O}_{(11)} \mathrm{O}_{(12)}$ stretch |
| $v_{15}$ | $\mathrm{A}^{\prime}$ | 985.0 | 968.0 | Methyl rock |
| $v_{16}$ | $\mathrm{A}^{\prime}$ | 798.6 | 787.2 | $\mathrm{C}_{(5)} \mathrm{C}_{(6)}$ stretch |
| $v_{17}$ | $\mathrm{A}^{\prime}$ | 640.4 | 629.2 | $\mathrm{C}_{(5)} \mathrm{O}_{(11)} \mathrm{O}_{(12)}$ in-plane bend |
| $v_{18}$ | $\mathrm{A}^{\prime}$ | 479.1 | 470.6 | $\mathrm{C}_{(5)} \mathrm{C}_{(6)} \mathrm{C}_{(8)}$ in-plane bend |
| $v_{19}$ | $\mathrm{A}^{\prime}$ | 326.0 | 328.3 | $\mathrm{C}_{(1)} \mathrm{C}_{(5)} \mathrm{O}_{(11)} \mathrm{O}_{(12)}$ in-plane bend |
| $v_{20}$ | $\mathrm{A}^{\prime}$ | 244.5 | 250.1 | $\mathrm{C}_{(8)} \mathrm{C}_{(6)} \mathrm{C}_{(5)} \mathrm{O}_{(11)}$ ring closing |
| $v_{21}$ | A" | 3110.9 | 2970.9 | Methyl out-of-phase CH stretch |
| $v_{22}$ | A" | 1486.0 | 1445.2 | Methyl out-of-plane CH wag |
| $v_{23}$ | A" | 1057.8 | 1031.5 | Methyl asymmetric scissor |
| $v_{24}$ | A" | 1049.8 | 1027.0 | Methine out-of-plane $\mathrm{C}_{(6)} \mathrm{H}_{(7)}$ wag |
| $v_{25}$ | A" | 977.5 | 958.8 | Vinyl out-of-plane $\mathrm{C}_{(8)} \mathrm{H}_{(9)} \mathrm{H}_{(10)}$ wag |
| $v_{26}$ | A" | 718.4 | 707.0 | $\mathrm{C}_{(5)} \mathrm{C}_{(6)} \mathrm{C}_{(8)}$ out-of-plane bend |
| $v_{27}$ | A" | 377.1 | 375.8 | $\mathrm{C}_{(8)} \mathrm{C}_{(6)} \mathrm{C}_{(5)} \mathrm{O}_{(11)}$ out-of-plane ring distortion |
| $v_{28}$ | A" | 280.6 | 275.0 | $\mathrm{C}_{(1)} \mathrm{C}_{(5)} \mathrm{O}_{(11)} \mathrm{O}_{(12)}$ out-of-plane bend |
| $v_{29}$ | A" | 149.8 | 162.7 | Vinyl torsion |


| $v_{30}$ | $A^{\prime}$ | 114.3 | 107.0 | Methyl torsion |
| :--- | :--- | :--- | :--- | :--- |

Table S8. Fundamental harmonic and anharmonic vibrational frequencies computed for the transition states (TS) associated with 1,4 H-atom transfer from syn-trans-MVK-OO to 2-hydroperoxy-buta-1,3diene (HPBD), the $1,4 \mathrm{H}$-atom transfer from syn-cis-MVK-OO to HPBD, and the ring closing reaction from anti-trans-MVK-OO to 5-methyl-3H-1,2-dioxole (dioxole) at the B2PLYP-D3/cc-pVTZ level of theory.

|  | syn-trans-MVK-OO TS |  | syn-cis-MVK-OO TS |  | anti-MVK-OO to <br> dioxole TS |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Mode | Harmonic <br> Frequency <br> $\left(\mathrm{cm}^{-1}\right)$ | Anharmonic <br> Frequency <br> $\left(\mathrm{cm}^{-1}\right)$ | Harmonic <br> Frequency <br> $\left(\mathrm{cm}^{-1}\right)$ | Anharmonic <br> Frequency <br> $\left(\mathrm{cm}^{-1}\right)$ | Harmonic <br> Frequency <br> $\left(\mathrm{cm}^{-1}\right)$ | Anharmonic <br> Frequency <br> $\left(\mathrm{cm}^{-1}\right)$ |
| $v_{1}$ | 3268.3 | 3125.4 | 3271.8 | 3132.8 | 3304.9 | 3162.7 |
| $v_{2}$ | 3217.9 | 3076.0 | 3211.3 | 3071.6 | 3189.7 | 3042.6 |
| $v_{3}$ | 3196.9 | 3047.4 | 3205.0 | 3075.2 | 3157.3 | 3016.1 |
| $v_{4}$ | 3175.0 | 3010.8 | 3177.2 | 3039.7 | 3125.9 | 2986.8 |
| $v_{5}$ | 3110.9 | 2958.7 | 3107.2 | 2953.5 | 3106.0 | 2942.1 |
| $v_{6}$ | 1839.5 | 1789.7 | 1844.0 | 1785.2 | 3061.7 | 2964.1 |
| $v_{7}$ | 1682.0 | 1642.2 | 1686.3 | 1642.0 | 1595.2 | 1552.9 |
| $v_{8}$ | 1548.2 | 1507.5 | 1534.3 | 1495.3 | 1540.1 | 1487.7 |
| $v_{9}$ | 1477.8 | 1430.6 | 1488.4 | 1448.1 | 1498.1 | 1456.4 |
| $v_{10}$ | 1466.9 | 1426.8 | 1436.5 | 1394.4 | 1486.9 | 1444.6 |
| $v_{11}$ | 1351.6 | 1315.7 | 1368.0 | 1326.7 | 1424.2 | 1389.7 |
| $v_{12}$ | 1346.9 | 1312.5 | 1347.8 | 1318.7 | 1384.0 | 1343.3 |
| $v_{13}$ | 1293.7 | 1259.7 | 1315.7 | 1285.5 | 1282.8 | 1248.0 |
| $v_{14}$ | 1067.7 | 1048.8 | 1086.6 | 1065.8 | 1243.2 | 1211.4 |
| $v_{15}$ | 1037.2 | 1011.7 | 1033.7 | 1014.8 | 1090.0 | 1067.2 |
| $v_{16}$ | 1027.0 | 1004.0 | 1025.5 | 1001.7 | 1056.2 | 1031.6 |
| $v_{17}$ | 989.8 | 968.9 | 989.8 | 969.9 | 1044.7 | 1022.6 |
| $v_{18}$ | 962.4 | 940.5 | 956.8 | 942.0 | 1043.0 | 1019.8 |
| $v_{19}$ | 938.1 | 913.0 | 944.5 | 924.8 | 959.4 | 941.2 |
| $v_{20}$ | 905.0 | 886.4 | 903.9 | 888.5 | 912.1 | 893.9 |
| $v_{21}$ | 757.7 | 727.2 | 751.8 | 725.5 | 808.2 | 794.1 |
| $v_{22}$ | 737.5 | 718.7 | 725.1 | 707.9 | 724.1 | 707.1 |
| $v_{23}$ | 635.3 | 624.7 | 646.5 | 635.0 | 638.2 | 629.9 |
| $v_{24}$ | 546.4 | 527.7 | 538.0 | 518.5 | 585.8 | 576.1 |
| $v_{25}$ | 494.5 | 486.5 | 496.6 | 490.0 | 520.7 | 513.3 |
| $v_{26}$ | 470.8 | 461.0 | 476.5 | 471.3 | 345.1 | 343.8 |
| $v_{27}$ | 275.9 | 271.5 | 266.0 | 258.4 | 267.8 | 259.6 |
| $v_{28}$ | 243.9 | 239.0 | 229.6 | 227.2 | 232.5 | 224.4 |
| $v_{29}$ | 121.3 | 121.9 | 81.7 | 78.7 | 130.0 | 111.5 |
| $v_{30}$ | $1629.5 i$ | $1769.1 i$ | $1621.3 i$ | $1763.5 i$ | $471.2 i$ | $484.9 i$ |

Table S9. Position, tentative conformer assignment, and peak intensity of the strongest features observed in the IR action spectrum of MVK-OO in the $2 v_{\mathrm{CH}}$ region from 5700 to $6300 \mathrm{~cm}^{-1}$.

| Position $\left(\mathrm{cm}^{-1}\right)$ | Conformer Assignment | Relative Intensity |
| :--- | :--- | :--- |
| 5869.6 | anti-cis and anti-trans | 0.60 |
| 5975.6 | syn-trans contribution | 0.89 |
| 6040.6 | mixed | 0.76 |
| 6174.4 | anti-trans | 0.63 |
| 6200.4 | syn-trans | 1.00 |
| 6234.2 | anti-cis | 0.36 |

Table S10. Experimentally measured rise rates $k_{\text {rise }}$ for appearance of OH products and corresponding rise times $\tau_{\text {rise }}$ arising from the unimolecular decay of IR activated MVK-OO Criegee intermediates with $\pm 1 \sigma$ uncertainties from repeated measurements and the fitting procedure (see Sec. S4). The exponential fall rates $k_{\text {fall }}$ and corresponding fall times $\tau_{\text {fall }}$ originate from molecules moving out of the spatial region irradiated by the UV probe laser.

| Energy $\left(\mathrm{cm}^{-1}\right)$ | $k_{\text {rise }}\left(\times 10^{6} \mathrm{~s}^{-1}\right)$ | $\tau_{\text {rise }}(\mathrm{ns})$ | $\left.k_{\text {fall }} \times 10^{6} \mathrm{~s}^{-1}\right)$ | $\tau_{\text {fall }}(\mathrm{ns})$ |
| :--- | :--- | :--- | :--- | :--- |
| 6200.4 | $2.3 \pm 0.2$ | $430 \pm 30$ | $0.69 \pm 0.02$ | $1450 \pm 50$ |
| 6174.2 | $3.2 \pm 0.4$ | $310 \pm 40$ | $0.61 \pm 0.04$ | $1600 \pm 100$ |
| 5975.4 | $1.4 \pm 0.3$ | $710 \pm 150$ | $0.72 \pm 0.06$ | $1390 \pm 110$ |

Table S11. Predicted RRKM rates $\left(\mathrm{s}^{-1}\right) k(E)$ from 5000 to $7000 \mathrm{~cm}^{-1}$ for the unimolecular decay of syn-MVK-OO to 2-hydroperoxybuta-1,3-diene ( $\left.\mathrm{CH}_{2}=\mathrm{CHC}\left(=\mathrm{CH}_{2}\right) \mathrm{OOH}, \mathrm{HPBD}\right)$, and for anti-MVK-OO to 5-methyl-3H-1,2-dioxole ( $\mathrm{CH}_{2} \mathrm{OOC}\left(\mathrm{CH}_{3}\right) \mathrm{CH}$, dioxole). Both calculations incorporate quantum mechanical tunneling via asymmetric Eckart ${ }^{\text {a }}$ and/or semi-classical transition state theory (SCTST) models.

| Energy <br> $\left(\mathrm{cm}^{-1}\right)$ | syn-trans-MVK-OO |  | syn-cis-MVK-OO |  | anti-trans-MVK-OO | anti-cis-MVK-OO |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | $1.39 \times 10^{5}$ | SCTART | $1.77 \times 10^{5}$ | Eckart | SCTST | Eckart |

[^2]Table S12. Hindered rotor fitting parameters (in $\mathrm{cm}^{-1}$ ) used for the vinyl torsional potential of syn-trans-MVK-OO, the syn-trans-MVK-OO transition state (TS) to 2-hydroperoxybuta-1,3-diene (HPBD), and anti-trans-MVK-OO. ${ }^{\text {a }}$

| Species | $\mathrm{V}_{0}$ | $\mathrm{~V}^{\mathrm{C}} 1-6$ | $\mathrm{~V}^{\mathrm{S}}{ }_{1-6}$ |
| :---: | :---: | :---: | :---: |
| syn-trans-MVK-OO | 1463 | $-153,-1248,-203,121,17,5$ | - |
| syn-trans-MVK-OO TS | 1074 | $-86,-925,-161,113,2,-17$ | $-56,151,-44,-51,9,0$ |
| anti-trans-MVK-OO | 1271 | $-239 .-1381,301,139,-76,-16$ | - |

${ }^{\mathrm{a}}$ These values are electronic energies (i.e., without ZPE corrections).

Table S13. The chemical names, formulas, and abbreviations for all species referenced in this work.

| Chemical Name | Chemical Formulas | Abbreviation | Labels |
| :---: | :---: | :---: | :---: |
| Z-1,3-diiodo-but-2-ene | Z-CH2(I)CHC(I)CH ${ }_{3}$ |  |  |
| E-1,3-diiodo-but-2-ene | E-CH2(I)CHC(I) $\mathrm{CH}_{3}$ |  |  |
| monoiodoalkene radical | $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{I}) \mathrm{CH}_{3}$ | Int(1) | $\operatorname{Int}(1)$ |
| iodoalkene peroxy radical | $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{I})(\mathrm{OO}) \mathrm{CH}_{3}$ | Int(2) | $\operatorname{Int}(2)$ |
| MVK-OO | $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{OO}) \mathrm{CH}_{3}$ |  |  |
| TS | syn-trans-MVK-OO to cis-HPBD |  | TS1 |
| cis-2-hydroperoxybuta-1,3-diene | $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{OOH}) \mathrm{CH}_{2}$ | cis-HPBD | 1 a |
| trans-2-hydroperoxybuta-1,3-diene | $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{OOH}) \mathrm{CH}_{2}$ | trans-HPBD | 1 b |
| cis-2-oxybuta-1,3-diene | $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{O}) \mathrm{CH}_{2}$ | cis-OBD | 2 a |
| trans-2-oxybuta-1,3-diene | $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{O}) \mathrm{CH}_{2}$ | trans-OBD | 2 b |
| Roaming complex (1) | $\mathrm{OH}+\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{O}) \mathrm{CH}_{2}$ | $\mathrm{RC}(1)$ | $\mathrm{RC}(1)$ |
| Roaming complex (2) | $\mathrm{OH}+\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{O}) \mathrm{CH}_{2}$ | $\mathrm{RC}(2)$ | RC(2) |
| 1-hydroxybut-3-en-2-one | $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{O}) \mathrm{CH}_{2} \mathrm{OH}$ | HB | 3 |
| 1-oxoprop-2-enyl | $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{O})$ |  | 4 |
| hydroxymethyl radical | $\mathrm{CH}_{2} \mathrm{OH}$ |  | 5 |
| trans-3-methyl-3-vinyldioxirane | $\mathrm{CH}_{2} \mathrm{CHC}(\mathrm{cyc}-\mathrm{OO}) \mathrm{CH}_{3}$ | trans-dioxirane | 6a |
| cis-3-methyl-3-vinyldioxirane | $\mathrm{CH}_{2} \mathrm{CHC}\left(\right.$ cyc-OO) $\mathrm{CH}_{3}$ | cis-dioxirane | 6 b |
| 3-hydroperoxybuta-1,2-diene | $\mathrm{CH}_{2} \mathrm{CC}(\mathrm{OOH}) \mathrm{CH}_{3}$ | AHP | 7 |
| 3-oxybuta-1,2-diene | $\mathrm{CH}_{2} \mathrm{CC}(\mathrm{O}) \mathrm{CH}_{3}$ | OA | 8 |
| 3-hydroperoxy-3-methylcycloprop- <br> 1-ene | cyc-CHCHC $(\mathrm{OOH}) \mathrm{CH}_{3}$ | CPHP | 9 |
| 3-methyl-3-oxycycloprop-1-ene | cyc-CHCHC(O)CH3 | OCP | 10 |
| 5-methyl-3H-1,2-dioxole | cyc- $\mathrm{CH}_{2} \mathrm{OOC}\left(\mathrm{CH}_{3}\right) \mathrm{CH}$ | dioxole | 11 |
| 1,3-dioxybut-2-ene | $\mathrm{OCH}_{2} \mathrm{CHC}(\mathrm{O}) \mathrm{CH}_{3}$ | diradical | 12 |
| 3-oxobutanal | $\mathrm{CH}(\mathrm{O}) \mathrm{CH}_{2} \mathrm{C}(\mathrm{O}) \mathrm{CH}_{3}$ | $\beta$-dicarbonyl | 13 |
| 3-hydroxybut-2-enal | $\mathrm{CH}(\mathrm{O}) \mathrm{CHCH}(\mathrm{OH}) \mathrm{CH}_{3}$ | enol | 14 |
| 1-oxobut-2-enyl | $\mathrm{CH}(\mathrm{O}) \mathrm{CHCHCH}_{2}$ | coproduct | 15 |

Table S14. Optimized geometries of stationary points at the B2PLYP-D3/cc-pVTZ level of theory.

| Single-Reference Stationary Points |  |  |  |
| :---: | :---: | :---: | :---: |
| Minima |  |  |  |
| syn-trans-MVK-OO |  |  |  |
| C | -0.281002 | -2.428825 | 0.000000 |
| C | 0.489860 | -1.332579 | 0.000000 |
| C | 0.000000 | 0.017627 | 0.000000 |
| C | -1.397431 | 0.477385 | 0.000000 |
| O | 0.934365 | 0.910720 | 0.000000 |
| O | 0.561182 | 2.203583 | 0.000000 |
| H | -1.359012 | -2.376515 | 0.000000 |
| H | 0.163693 | -3.411629 | 0.000000 |
| H | 1.567972 | -1.424436 | 0.000000 |
| H | -2.098829 | -0.348501 | 0.000000 |
| H | -1.553379 | 1.122502 | 0.866535 |
| H | -1.553379 | 1.122502 | -0.866535 |
| syn-cis-MVK-OO |  |  |  |
| C | -0.796268 | -1.572469 | 0.000000 |
| C | 0.000000 | -0.334198 | 0.000000 |
| C | 1.445692 | -0.280313 | 0.000000 |
| C | 2.181733 | 0.838790 | 0.000000 |
| O | -0.625501 | 0.789499 | 0.000000 |
| O | -1.976517 | 0.749769 | 0.000000 |
| H | -1.462580 | -1.565240 | 0.865297 |
| H | -1.462580 | -1.565240 | -0.865297 |
| H | -0.162827 | -2.453197 | 0.000000 |
| H | 1.934144 | -1.244681 | 0.000000 |
| H | 3.259177 | 0.786700 | 0.000000 |
| H | 1.723866 | 1.816655 | 0.000000 |
| anti-trans-MVK-OO |  |  |  |
| C | -1.894146 | -1.185090 | 0.000000 |
| C | -0.571837 | -0.965527 | 0.000000 |
| C | 0.000000 | 0.349961 | 0.000000 |
| C | -0.769734 | 1.622704 | 0.000000 |
| O | 1.282506 | 0.506388 | 0.000000 |
| O | 2.101575 | -0.560185 | 0.000000 |
| H | -2.612894 | -0.378124 | 0.000000 |
| H | -2.286939 | -2.190359 | 0.000000 |
| H | 0.144815 | -1.772424 | 0.000000 |
| H | -0.083752 | 2.464487 | 0.000000 |
| H | -1.409789 | 1.687253 | 0.880050 |
| H | -1.409789 | 1.687253 | -0.880050 |


| anti-cis-MVK-OO |  |  |  |
| :---: | :---: | :---: | :---: |
| C | -1.352990 | -1.521124 | 0.000000 |
| C | -1.214381 | -0.180848 | 0.000000 |
| C | 0.000000 | 0.576665 | 0.000000 |
| C | -0.021963 | 2.069054 | 0.000000 |
| O | 1.191358 | 0.084982 | 0.000000 |
| O | 1.382201 | -1.251687 | 0.000000 |
| H | -0.494812 | -2.166647 | 0.000000 |
| H | -2.348757 | -1.942692 | 0.000000 |
| H | -2.104292 | 0.435798 | 0.000000 |
| H | 0.990778 | 2.459965 | 0.000000 |
| H | -0.547687 | 2.442365 | 0.879064 |
| H | -0.547687 | 2.442365 | -0.879064 |
| trans-HPBD (1b) |  |  |  |
| C | -2.190756 | -0.692912 | -0.003071 |
| C | -1.445754 | 0.413306 | 0.020214 |
| C | 0.013806 | 0.455029 | -0.002236 |
| C | 0.721715 | 1.588008 | -0.003222 |
| O | 0.539944 | -0.815903 | -0.022748 |
| O | 1.979630 | -0.777544 | -0.088691 |
| H | 2.195300 | -1.033111 | 0.818326 |
| H | -1.747752 | -1.675824 | -0.043861 |
| H | -3.267941 | -0.629017 | 0.014193 |
| H | -1.915634 | 1.386564 | 0.056377 |
| H | 0.189628 | 2.524463 | 0.015143 |
| H | 1.795734 | 1.593910 | -0.038780 |
| cis-HPBD (1b) |  |  |  |
| C | -2.46435 | -0.11691 | 0.238336 |
| C | -1.30033 | -0.56969 | -0.22339 |
| C | -0.02344 | 0.144293 | -0.09618 |
| C | 0.153909 | 1.464923 | -0.12118 |
| O | 0.974393 | -0.80084 | 0.028511 |
| O | 2.277865 | -0.18151 | 0.024577 |
| H | 2.519831 | -0.29743 | 0.953085 |
| H | -2.53391 | 0.816122 | 0.778558 |
| H | -3.37592 | -0.67386 | 0.08375 |
| H | -1.24838 | -1.52866 | -0.72279 |
| H | -0.70304 | 2.098371 | -0.2745 |
| H | 1.128601 | 1.908518 | -0.02833 |
| dioxole (11) |  |  |  |
| C | -2.167553 | 0.060489 | -0.004807 |
| C | -0.683232 | 0.125915 | -0.003925 |


| C | 0.170081 | 1.143757 | -0.033828 |
| :---: | :---: | :---: | :---: |
| C | 1.554460 | 0.584898 | 0.051521 |
| O | -0.085539 | -1.098560 | 0.054088 |
| O | 1.362919 | -0.838086 | -0.081663 |
| H | -2.525051 | -0.449745 | 0.888636 |
| H | -2.582146 | 1.063800 | -0.028217 |
| H | -2.524516 | -0.494143 | -0.871307 |
| H | -0.084916 | 2.186780 | -0.064608 |
| H | 2.044633 | 0.802223 | 1.007160 |
| H | 2.210411 | 0.893894 | -0.764831 |
| trans-dioxirane (6a) |  |  |  |
| C | -2.193128 | -0.118205 | 0.000054 |
| C | -0.991517 | -0.686364 | -0.000202 |
| C | 0.292535 | 0.052755 | -0.000325 |
| C | 0.301344 | 1.551185 | -0.000067 |
| O | 1.306590 | -0.564402 | 0.752573 |
| O | 1.307066 | -0.564640 | -0.752208 |
| H | -2.320131 | 0.954471 | 0.000072 |
| H | -3.091059 | -0.717259 | 0.000276 |
| H | -0.874974 | -1.761456 | -0.000224 |
| H | 1.332107 | 1.890559 | 0.000195 |
| H | -0.205400 | 1.934613 | 0.883630 |
| H | -0.205197 | 1.935184 | -0.883622 |
| cis-dioxirane (6b) |  |  |  |
| C | 2.120367 | 0.068618 | -0.156720 |
| C | 1.013764 | 0.650541 | 0.290428 |
| C | -0.349228 | 0.104967 | 0.040793 |
| C | -1.436356 | 1.104937 | -0.222090 |
| O | -0.422180 | -1.088406 | -0.677375 |
| O | -0.729168 | -1.019001 | 0.799371 |
| H | 2.070688 | -0.848769 | -0.724008 |
| H | 3.093178 | 0.494258 | 0.037865 |
| H | 1.057458 | 1.575442 | 0.850922 |
| H | -2.375350 | 0.584036 | -0.381313 |
| H | -1.192243 | 1.699773 | -1.101265 |
| H | -1.534227 | 1.780138 | 0.627362 |
| $\beta$-dicarbonyl (13) |  |  |  |
| C | 1.743964 | 1.073828 | -0.21401 |
| C | 0.963217 | -0.17549 | 0.090426 |
| C | -0.35719 | 0.006638 | 0.832659 |
| C | -1.49648 | -0.31737 | -0.11229 |
| O | 1.318184 | -1.28059 | -0.25868 |


| O | -2.39155 | 0.447851 | -0.3713 |
| :---: | :---: | :---: | :---: |
| H | 2.629156 | 0.831181 | -0.79263 |
| H | 2.028894 | 1.56677 | 0.716326 |
| H | 1.114237 | 1.775609 | -0.76304 |
| H | -0.37545 | -0.72698 | 1.6401 |
| H | -0.49308 | 1.009076 | 1.228139 |
| H | -1.43799 | -1.31945 | -0.5697 |
| enol (14) |  |  |  |
| C | -0.24049 | 2.233299 | 0.000000 |
| C | 0.00000 | 0.76417 | 0.000000 |
| C | -0.99105 | -0.1811 | 0.000000 |
| C | -0.65142 | -1.56899 | 0.000000 |
| O | 1.278813 | 0.427663 | 0.000000 |
| O | 0.51517 | -1.99721 | 0.000000 |
| H | -1.30168 | 2.460774 | 0.000000 |
| H | 0.22622 | 2.679232 | 0.877607 |
| H | 0.22622 | 2.679232 | -0.877607 |
| H | -2.02523 | 0.119566 | 0.000000 |
| H | -1.47891 | -2.2914 | 0.000000 |
| H | 1.299274 | -0.5753 | 0.000000 |
| HB (3) |  |  |  |
| C | -2.11344 | 1.34788 | 0.000000 |
| C | -1.47823 | 0.17722 | 0.000000 |
| C | 0.00000 | 0.101853 | 0.000000 |
| C | 0.617229 | -1.279 | 0.000000 |
| O | 0.724608 | 1.08313 | 0.000000 |
| O | 2.012599 | -1.22058 | 0.000000 |
| H | -1.54703 | 2.268384 | 0.000000 |
| H | -3.1911 | 1.409405 | 0.000000 |
| H | -2.02372 | -0.75746 | 0.000000 |
| H | 0.242648 | -1.81678 | 0.879399 |
| H | 0.242648 | -1.81678 | -0.879399 |
| H | 2.225588 | -0.27494 | 0.000000 |
| trans-OBD (2b) |  |  |  |
| C | -0.356578 | -1.919984 | 0.000000 |
| C | 0.491474 | -0.895553 | 0.000000 |
| C | 0.000000 | 0.512914 | 0.000000 |
| C | 0.992209 | 1.556566 | 0.000000 |
| O | -1.199848 | 0.786165 | 0.000000 |
| O | -1.421324 | -1.734061 | 0.000000 |
| H | -0.012245 | -2.943035 | 0.000000 |
| H | 1.561337 | -1.056632 | 0.000000 |


| H | 2.049096 | 1.338522 | 0.000000 |
| :---: | :---: | :---: | :---: |
| H | 0.659292 | 2.58222 | 0.000000 |
| H | -0.356578 | -1.919984 | 0.000000 |
| H | 0.491474 | -0.895553 | 0.000000 |
| cis-OBD (2b) |  |  |  |
| C | -0.220053 | -1.927731 | 0.000000 |
| C | -0.750286 | -0.706992 | 0.000000 |
| C | 0.000000 | 0.578346 | 0.000000 |
| C | 1.442971 | 0.580467 | 0.000000 |
| O | -0.622894 | 1.639096 | 0.000000 |
| O | 0.846435 | -2.097946 | 0.000000 |
| H | -0.848585 | -2.805895 | 0.000000 |
| H | -1.823569 | -0.571873 | 0.000000 |
| H | 2.035139 | -0.319579 | 0.000000 |
| H | 1.937945 | 1.537985 | 0.000000 |
| H | -0.220053 | -1.927731 | 0.000000 |
| H | -0.750286 | -0.706992 | 0.000000 |
| AHP (7) |  |  |  |
| C | 2.317255 | -0.08213 | -0.008589 |
| C | 1.034673 | 0.155715 | 0.013236 |
| C | -0.23792 | 0.453645 | 0.003115 |
| C | -0.81849 | 1.832443 | -0.002134 |
| O | -1.26718 | -0.47526 | 0.018225 |
| O | -0.74616 | -1.81163 | -0.116279 |
| H | 2.892995 | -0.18542 | 0.903526 |
| H | 2.857427 | -0.19196 | -0.941420 |
| H | -0.02078 | 2.568205 | 0.012381 |
| H | -1.42628 | 1.979665 | -0.894237 |
| H | -1.45574 | 1.981111 | 0.869162 |
| H | -0.51405 | -2.01453 | 0.801259 |
| Transition States |  |  |  |
| syn-trans to syn-cis-MVK-OO |  |  |  |
| C | 2.327858 | -0.267919 | 0.425627 |
| C | 1.381300 | -0.133215 | -0.497496 |
| C | -0.027092 | 0.153355 | -0.167281 |
| C | -0.602629 | 1.490867 | 0.045170 |
| O | -0.796694 | -0.864200 | -0.093452 |
| O | -2.103652 | -0.635657 | 0.189406 |
| H | 2.105556 | -0.189953 | 1.480296 |
| H | 3.351766 | -0.466552 | 0.146356 |
| H | 1.626162 | -0.217122 | -1.550508 |
| H | -1.070284 | 1.516480 | 1.033036 |


| H | -1.432790 | 1.629417 | -0.652467 |
| :---: | :---: | :---: | :---: |
| H | 0.145734 | 2.268058 | -0.060451 |
| anti-trans to anti-cis-MVK-OO |  |  |  |
| C | 2.007829 | -0.418699 | -0.342971 |
| C | 0.984974 | -0.461235 | 0.502459 |
| C | -0.412755 | -0.301218 | 0.080860 |
| C | -1.331026 | -1.454707 | -0.099639 |
| O | -0.925829 | 0.850993 | -0.119854 |
| O | -0.181649 | 1.963910 | 0.046691 |
| H | 1.863784 | -0.218324 | -1.394427 |
| H | 3.019565 | -0.567451 | 0.002037 |
| H | 1.146198 | -0.648731 | 1.558247 |
| H | -2.328717 | -1.110049 | -0.356799 |
| H | -1.377214 | -2.045749 | 0.816530 |
| H | -0.957925 | -2.113760 | -0.884538 |
| syn-trans-MVK-OO to cis-HPBD (1a) |  |  |  |
| C | 2.457115 | 0.070170 | 0.032784 |
| C | 1.316473 | -0.618112 | -0.055817 |
| C | 0.010731 | -0.001078 | 0.060352 |
| C | -0.383451 | 1.346869 | -0.052273 |
| O | -0.977463 | -0.869354 | 0.073675 |
| O | -2.202077 | -0.190060 | -0.031532 |
| H | 2.460619 | 1.133723 | 0.220400 |
| H | 3.411786 | -0.420028 | -0.080885 |
| H | 1.320065 | -1.687395 | -0.219937 |
| H | -1.560158 | 0.884857 | -0.502121 |
| H | -0.952622 | 1.745026 | 0.784583 |
| H | 0.351428 | 2.032029 | -0.449460 |
| syn-cis-MVK-OO to trans-HPBD (1b) |  |  |  |
| C | 2.297324 | -0.481816 | 0.019876 |
| C | 1.411571 | 0.515143 | -0.053642 |
| C | -0.026106 | 0.342616 | 0.063494 |
| C | -1.022147 | 1.338205 | 0.014306 |
| O | -0.472178 | -0.889564 | 0.025294 |
| O | -1.877499 | -0.876092 | -0.057740 |
| H | 1.982914 | -1.505554 | 0.158002 |
| H | 3.356161 | -0.285350 | -0.047200 |
| H | 1.739610 | 1.538093 | -0.170472 |
| H | -1.833037 | 0.412863 | -0.487093 |
| H | -1.712231 | 1.363363 | 0.854875 |
| H | -0.699849 | 2.316944 | -0.312739 |
| anti-trans-MVK-OO to AHP (7) |  |  |  |


| C | 2.151385 | -0.445532 | 0.103605 |
| :---: | :---: | :---: | :---: |
| C | 0.867444 | -0.403392 | -0.248881 |
| C | -0.193126 | 0.449890 | 0.011178 |
| C | -0.258580 | 1.932903 | -0.037375 |
| O | -1.359166 | -0.158820 | 0.075984 |
| O | -1.143157 | -1.557896 | 0.061771 |
| H | 2.554882 | 0.147431 | 0.918113 |
| H | 2.840727 | -1.126395 | -0.378015 |
| H | 0.010008 | -1.410457 | -0.470817 |
| H | -1.291653 | 2.270514 | -0.053087 |
| H | 0.256173 | 2.297740 | -0.923374 |
| H | 0.245707 | 2.351680 | 0.833978 |
| anti-cis-MVK-OO to dioxole (11) |  |  |  |
| C | 2.113823 | 0.224472 | 0.046960 |
| C | 0.631136 | 0.106616 | 0.056598 |
| C | -0.289484 | 1.134011 | 0.002167 |
| C | -1.658696 | 0.880700 | 0.034722 |
| O | 0.192038 | -1.122782 | -0.127554 |
| O | -1.177527 | -1.228705 | 0.016537 |
| H | 2.550605 | -0.538418 | -0.594098 |
| H | 2.411928 | 1.209438 | -0.302360 |
| H | 2.509711 | 0.088426 | 1.053507 |
| H | 0.081305 | 2.079491 | -0.370189 |
| H | -2.293385 | 1.513012 | -0.583405 |
| H | -2.156925 | 0.385158 | 0.842006 |
| anti-cis-MVK-OO to cis-dioxirane (6b) TS |  |  |  |
| C | -2.021813 | -0.504220 | 0.066142 |
| C | -0.772895 | -0.926485 | -0.157005 |
| C | 0.478151 | -0.184962 | -0.104387 |
| C | 1.732682 | -0.895539 | 0.256821 |
| O | 0.664982 | 1.023218 | -0.558683 |
| O | -0.289251 | 1.580768 | 0.388537 |
| H | -2.202691 | 0.480833 | 0.459905 |
| H | -2.855955 | -1.160098 | -0.141277 |
| H | -0.616820 | -1.963706 | -0.436515 |
| H | 2.528149 | -0.603905 | -0.428757 |
| H | 1.618364 | -1.974479 | 0.289388 |
| H | 2.026357 | -0.543301 | 1.249006 |
| cis-dioxirane (6b) to syn-cis-MVK-OO TS |  |  |  |
| C | 2.165039 | -0.322011 | 0.141198 |
| C | 1.233476 | 0.635557 | 0.038240 |
| C | -0.161890 | 0.293356 | -0.141936 |


| C | -1.215421 | 1.332792 | 0.022053 |
| :---: | :---: | :---: | :---: |
| O | -0.404167 | -0.898510 | -0.592133 |
| O | -1.383390 | -1.185067 | 0.456755 |
| H | 1.878474 | -1.362624 | 0.114932 |
| H | 3.209177 | -0.079577 | 0.269266 |
| H | 1.489252 | 1.682042 | 0.127982 |
| H | -2.165861 | 0.950185 | -0.329890 |
| H | -0.911319 | 2.229328 | -0.525416 |
| H | -1.326492 | 1.611097 | 1.068825 |
| anti-trans-MVK-OO to trans-dioxirane (6a) |  |  |  |
| C | 2.121961 | -0.495037 | 0.088147 |
| C | 0.842625 | -0.704796 | -0.256568 |
| C | -0.188625 | 0.295382 | -0.161100 |
| C | 0.056753 | 1.726440 | 0.143306 |
| O | -1.423958 | 0.000452 | -0.453362 |
| O | -1.460560 | -1.086226 | 0.521949 |
| H | 2.455704 | 0.424359 | 0.544928 |
| H | 2.861675 | -1.267907 | -0.051852 |
| H | 0.509868 | -1.655769 | -0.642517 |
| H | -0.622631 | 2.331462 | -0.455041 |
| H | 1.084313 | 2.031623 | -0.017288 |
| H | -0.209078 | 1.890489 | 1.190366 |
| trans-dioxirane (6a) to syn-trans-MVK-OO TS |  |  |  |
| C | 2.293994 | -0.067922 | 0.253035 |
| C | 1.156752 | -0.693624 | -0.075004 |
| C | -0.121858 | -0.021638 | -0.190702 |
| C | -0.232499 | 1.467526 | -0.194199 |
| O | -1.125282 | -0.801728 | -0.460710 |
| O | -1.934844 | -0.227034 | 0.616148 |
| H | 2.322410 | 0.993245 | 0.450993 |
| H | 3.221729 | -0.611860 | 0.346655 |
| H | 1.134351 | -1.763182 | -0.232171 |
| H | -1.237556 | 1.742857 | -0.489675 |
| H | 0.512890 | 1.884188 | -0.875154 |
| H | -0.051155 | 1.878798 | 0.797070 |
| cis-dioxirane (6b) to trans-dioxirane (6a) |  |  |  |
| C | 2.143516 | -0.048353 | 0.246926 |
| C | 1.084544 | -0.217522 | -0.534446 |
| C | -0.313201 | 0.066186 | -0.089924 |
| C | -0.725825 | 1.506082 | -0.002201 |
| O | -1.282553 | -0.82472 | -0.559846 |
| O | -0.848532 | -0.784435 | 0.886513 |


| H | 2.046302 | 0.296379 | 1.267273 |
| :---: | :---: | :---: | :---: |
| H | 3.140229 | -0.266843 | -0.104687 |
| H | 1.187965 | -0.577299 | -1.549626 |
| H | -1.76708 | 1.565409 | 0.300634 |
| H | -0.594303 | 1.990373 | -0.968796 |
| H | -0.098639 | 2.026861 | 0.719736 |
| $\beta$-dicarbonyl (13) to enol (14) |  |  |  |
| C | -2.03396 | -0.88967 | -0.238730 |
| C | -0.95902 | 0.064983 | 0.122478 |
| C | 0.357017 | -0.19524 | 0.633537 |
| C | 1.473626 | 0.078981 | -0.289131 |
| O | -1.101 | 1.326534 | -0.025496 |
| O | 2.609491 | -0.31254 | -0.123832 |
| H | -2.97885 | -0.38112 | -0.399164 |
| H | -2.13595 | -1.63364 | 0.550344 |
| H | -1.74259 | -1.42756 | -1.141924 |
| H | 0.546415 | -0.98818 | 1.345095 |
| H | 1.204985 | 0.711647 | -1.157541 |
| H | 0.012091 | 1.252602 | 0.628896 |
| Multireference Stationary Points |  |  |  |
| HPBD dissociation |  |  |  |
| trans-HPBD (1b) to RC(1) TS |  |  |  |
| C | -0.12177 | -0.12177 | -0.121772 |
| C | 0.181151 | 0.181151 | 0.181151 |
| C | -0.10617 | -0.10617 | -0.106172 |
| C | 0.384358 | 0.384358 | 0.384358 |
| O | -0.77468 | -0.77468 | -0.774682 |
| H | -0.58073 | -0.58073 | -0.580734 |
| H | 0.101276 | 0.101276 | 0.101276 |
| H | 0.667745 | 0.667745 | 0.667745 |
| H | 0.907146 | 0.907146 | 0.907146 |
| H | 0.207172 | 0.207172 | 0.207172 |
| O | 0.458378 | 0.458378 | 0.458378 |
| H | -0.30435 | -0.30435 | -0.304350 |
| RC(1) |  |  |  |
| C | 0.00000 | -1.85192 | -0.298037 |
| C | 0.00000 | -1.17814 | 0.860903 |
| C | 0.00000 | 0.302122 | 0.921470 |
| C | 0.00000 | 0.921287 | 2.211567 |
| O | 0.00000 | 1.015945 | -0.100131 |
| H | 0.00000 | -1.33718 | -1.246924 |
| H | 0.00000 | -2.93078 | -0.306654 |


| H | 0.00000 | -1.70592 | 1.804363 |
| :---: | :---: | :---: | :---: |
| H | 0.00000 | 0.337327 | 3.118117 |
| H | 0.00000 | 1.997981 | 2.266412 |
| O | 0.00000 | 0.520816 | -2.905882 |
| H | 0.00000 | 0.773762 | -1.961570 |
| $\mathrm{RC}(1)$ to $\mathrm{RC}(2) \mathrm{TS}$ |  |  |  |
| C | 0.00000 | 1.804965 | -1.424791 |
| C | 0.00000 | 0.498778 | -1.721884 |
| C | 0.00000 | -0.52906 | -0.652853 |
| C | 0.00000 | -1.90833 | -1.031955 |
| O | 0.00000 | -0.20972 | 0.549404 |
| H | 0.00000 | 2.122048 | -0.392674 |
| H | 0.00000 | 2.557898 | -2.196869 |
| H | 0.00000 | 0.157652 | -2.747410 |
| H | 0.00000 | -2.20842 | -2.067794 |
| H | 0.00000 | -2.6572 | -0.256332 |
| O | 0.00000 | 0.305656 | 3.405617 |
| H | 0.00000 | 0.097867 | 2.455401 |
| RC(2) |  |  |  |
| C | 0.00000 | 0.764753 | -2.519264 |
| C | 0.00000 | -0.35675 | -1.786717 |
| C | 0.00000 | -0.30861 | -0.305078 |
| C | 0.00000 | -1.54429 | 0.415302 |
| O | 0.00000 | 0.782543 | 0.300606 |
| H | 0.00000 | 1.72725 | -2.030292 |
| H | 0.00000 | 0.732207 | -3.597237 |
| H | 0.00000 | -1.33071 | -2.255115 |
| H | 0.00000 | -2.48914 | -0.104515 |
| H | 0.00000 | -1.52119 | 1.493847 |
| O | 0.00000 | 0.439478 | 3.121107 |
| H | 0.00000 | 0.701953 | 2.177467 |
| $\mathrm{RC}(2)$ to HB (3) TS |  |  |  |
| C | -1.43578 | 0.14639 | 0.575506 |
| C | -0.26605 | 0.141701 | -0.252747 |
| O | 0.854714 | 0.40249 | 0.227043 |
| H | 0.789567 | 0.018462 | 2.094713 |
| O | 0.416796 | -0.31049 | 2.937211 |
| H | -1.355 | 0.458701 | 1.604523 |
| H | -2.39483 | -0.14737 | 0.178850 |
| C | -0.42735 | -0.17559 | -1.691815 |
| C | 0.62516 | -0.19613 | -2.520308 |
| H | -1.42481 | -0.38857 | -2.049092 |


| H | 1.612576 | 0.020007 | -2.141121 |
| :---: | :---: | :---: | :---: |
| H | 0.511762 | -0.42499 | -3.568093 |
| syn to anti-MVK-OO torsional isomerization |  |  |  |
| syn-cis to anti-cis-MVK-OO TS |  |  |  |
| C | 0.034644 | 0.14401 | -2.134649 |
| C | -0.13773 | -0.77752 | -1.116141 |
| C | 0.07295 | -0.53489 | 0.227222 |
| C | -0.08801 | -1.46339 | 1.367497 |
| O | 0.553006 | 0.744493 | 0.602520 |
| O | -0.4234 | 1.599812 | 0.732010 |
| H | 0.354911 | 1.151909 | -1.926714 |
| H | -0.14966 | -0.13456 | -3.158729 |
| H | -0.46617 | -1.77802 | -1.362894 |
| H | -0.39177 | -2.44621 | 1.018527 |
| H | 0.845856 | -1.55892 | 1.922219 |
| H | -0.84252 | -1.08476 | 2.058497 |
| syn-trans to anti-trans-MVK-OO TS |  |  |  |
| C | 0.182719 | -0.436631 | -2.394948 |
| C | -0.123851 | -0.702045 | -1.070505 |
| C | -0.167422 | 0.233953 | -0.057239 |
| C | 0.085094 | 1.690424 | -0.090552 |
| O | -0.538913 | -0.247774 | 1.225642 |
| O | 0.511739 | -0.581744 | 1.921702 |
| H | 0.422169 | 0.557803 | -2.736259 |
| H | 0.190420 | -1.231711 | -3.121716 |
| H | -0.352461 | -1.718678 | -0.780648 |
| H | 0.288989 | 2.030380 | -1.100843 |
| H | -0.777806 | 2.233203 | 0.295340 |
| H | 0.939589 | 1.933532 | 0.541979 |
| dioxole reaction |  |  |  |
| dioxole (11) to diradical (12) TS |  |  |  |
| C | -2.22083 | 0.131219 | 0.082699 |
| C | -0.7215 | 0.015663 | -0.080404 |
| C | 0.15012 | 1.072409 | -0.118275 |
| C | 1.565835 | 0.613275 | 0.067374 |
| O | -0.22308 | -1.18042 | -0.070393 |
| O | 1.612887 | -0.76866 | 0.043779 |
| H | -2.53765 | 1.176805 | 0.073860 |
| H | -2.73118 | -0.40231 | -0.725711 |
| H | -2.52524 | -0.32986 | 1.028263 |
| H | -0.13684 | 2.11667 | -0.110040 |


| H | 2.182737 | 1.011861 | -0.767837 |
| :---: | :---: | :---: | :---: |
| H | 1.987896 | 1.024048 | 1.006013 |
| C diradical (12) |  |  |  |
| C | 0.17351 | 0.363102 | -2.344859 |
| C | -0.02514 | -0.07778 | -0.903765 |
| C | -0.03412 | 0.965483 | 0.116364 |
| O | -0.22039 | 0.645118 | 1.564788 |
| H | -0.20946 | -1.26272 | -0.599224 |
| H | 0.311246 | -0.5155 | 2.045783 |
| H | 1.154957 | 0.852739 | -2.461166 |
| H | 0.120041 | -0.51332 | -3.005231 |
| H | -0.59856 | 1.093901 | -2.638261 |
| H | -0.01774 | 2.019336 | -0.186075 |
|  | 0.288729 | 1.424189 | 2.179526 |
| C | -1.29847 | 0.756729 | 1.828047 |
| C | diradical (12) to $\beta$-dicarbonyl (13) |  |  |
| C | 0.017477 | 0.857923 | -2.264513 |
| O | -0.00306 | -0.05288 | -1.062836 |
| H | -0.02787 | 0.565243 | 0.244997 |
| H | -0.03913 | -0.26235 | 1.458112 |
| H | 0.014935 | -1.28133 | -1.181762 |
| H | 0.062811 | 0.258042 | 2.682272 |
| H | -0.17505 | 0.277058 | -3.160210 |
| H | 0.994974 | -2.353093 |  |
|  | -0.72192 | -2.162434 |  |
|  | -0.14448 | 1.649835 | 0.342702 |
|  | -1.08569 | 1.635968 | 1.508419 |
| 0.524549 | -0.65531 | 1.361532 |  |

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[^1]:    ${ }^{\text {a }}$ Without ZPE correction.
    ${ }^{\mathrm{b}}$ Including ZPE correction.
    ${ }^{\mathrm{c}} \mathrm{T} 1$ diagnostic for the ion state.

[^2]:    ${ }^{\text {a }}$ Barriers include ZPE corrections.

