Negative-Ion Photoelectron Spectroscopy, Gas-Phase Acidity, and Thermochemistry of the Peroxy Radicals CH$_3$OO and CH$_3$CH$_2$OO

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Abstract: Methyl, methyl-$d_3$, and ethyl hydroperoxide anions (CH$_3$OO$^-$, CD$_3$OO$^-$, and CH$_3$CH$_2$OO$^-$) have been prepared by deprotonation of their respective hydroperoxides in a stream of helium buffer gas. Photodetachment with 364 nm (3.408 eV) radiation was used to measure the adiabatic electron affinities: $E_A$(CH$_3$OO, X $^2$A') = 1.161 ± 0.005 eV, $E_A$(CD$_3$OO, X $^2$A') = 1.154 ± 0.004 eV, and $E_A$(CH$_3$CH$_2$OO, X $^2$A') = 1.186 ± 0.004 eV. The photoelectron spectra yield values for the term energies: $\Delta E$(X $^2$A'-A $^2$A')-[CH$_3$OO] = 0.914 ± 0.005 eV, $\Delta E$(X $^2$A'-A $^2$A')-[CD$_3$OO] = 0.913 ± 0.004 eV, and $\Delta E$(X $^2$A'-A $^2$A')-[CH$_3$CH$_2$OO] = 0.938 ± 0.004 eV. A localized RO-O stretching mode was observed near 1100 cm$^{-1}$ for the ground state of all three radicals, and low-frequency R-O-O bending modes are also reported. Proton-transfer kinetics of the hydroperoxides have been measured in a tandem flowing afterglow-selected ion flow tube (FA-SIFT) to determine the gas-phase acidity of the parent hydroperoxides: $\Delta_{acid}G_{298}$(CH$_3$OOH) = 367.6 ± 0.7 kcal mol$^{-1}$, $\Delta_{acid}G_{298}$(CD$_3$OOH) = 367.9 ± 0.9 kcal mol$^{-1}$, and $\Delta_{acid}G_{298}$(CH$_3$CH$_2$OOH) = 363.9 ± 2.0 kcal mol$^{-1}$. From these acidities we have derived the enthalpies of deprotonation: $\Delta H_{298}$(CH$_3$OOH) = 376.4 ± 1.0 kcal mol$^{-1}$, $\Delta H_{298}$(CD$_3$OOH) = 374.9 ± 1.1 kcal mol$^{-1}$, and $\Delta H_{298}$(CH$_3$CH$_2$OOH) = 371.0 ± 2.2 kcal mol$^{-1}$. Use of the negative-ion acidity/EA cycle provides the ROO $^+$ bond enthalpies: $\Delta H_{298}$(CH$_3$OOH$^-$) = 87.8 ± 1.0 kcal mol$^{-1}$, $\Delta H_{298}$(CH$_3$CH$_2$OOH$^-$) = 84.8 ± 2.2 kcal mol$^{-1}$. We review the thermochemistry of the peroxyl radicals, CH$_3$OO and CH$_3$CH$_2$OO. Using experimental bond enthalpies, $\Delta H_{298}$(ROO $^+$) and CBS/APNO ab initio electronic structure calculations for the energies of the corresponding hydroperoxides, we derive the heats of formation of the peroxyl radicals. The “electron affinity/acidity/CBS” cycle yields $\Delta H_{298}$(CH$_3$OO) = 4.8 ± 1.2 kcal mol$^{-1}$ and $\Delta H_{298}$(CH$_3$CH$_2$OO) = −6.8 ± 2.3 kcal mol$^{-1}$.

Introduction

Alkyl peroxy radicals (ROO) are generally the first oxidation products of saturated hydrocarbons in the troposphere.1–3 Atmospheric hydrocarbons react with strong oxidizers such as HO, O$_3$, or NO$_3$. The HO radical reacts with saturated hydrocarbons by H atom abstraction.2 The nascent alkyl radical, R, combines rapidly with atmospheric O$_2$ in a three-body reaction to produce the corresponding alkyl peroxy radical.1

\begin{align*}
\text{RH} + \text{OH} & \rightarrow \text{R} + \text{H}_2\text{O} \quad (1) \\
\text{R} + \text{O}_2 + \text{M} & \rightarrow \text{ROO} + \text{M} \quad (2)
\end{align*}

Atmospheric peroxy radicals react quickly with NO to generate NO$_2$, which is photodissociated by sunlight to produce NO and O ($^3P$). The latter is primarily responsible for the formation of tropospheric ozone (reactions 3–5).5 Given that NO and hydrocarbons are both byproducts of combustion, reactions 1–5 form a crucial part of the chemistry responsible for the formation of photochemical smog in industrialized areas.

\begin{align*}
\text{ROO} + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \quad (3) \\
\text{NO}_2 + \text{sunlight} & \rightarrow \text{NO} + \text{O} \left( ^3P \right) \quad (4) \\
\text{O}_2 + \text{O} \left( ^3P \right) + \text{M} & \rightarrow \text{O}_3 + \text{M} \quad (5)
\end{align*}

Alkyl peroxy radicals are also known to play a role in the chemistry of combustion.6 Under some conditions, particularly at low

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combustion temperatures (<700 K), hydrocarbon fuels can undergo a series of facile radical reactions involving the intermediary of alkyl peroxyl radicals. In an internal combustion engine such chemistry may result in accelerated ignition and indeed premature ignition. This phenomenon is referred to as autoignition or “engine knock” and has practical ramifications for engine wear and efficiency.7

\[ \text{RCH}_2\text{CH}_3 + \text{O}_2 \xrightarrow{\Delta} \text{RCH}_2\text{CH}_2 + \text{HO}_2 \] (6)

\[ \text{RCH}_2\text{CH}_2 + \text{O}_2 \rightarrow \text{RCH}_2\text{CH}_2\text{OO} \rightarrow \text{RCH} = \text{CH}_2 + \text{HO}_2 \] (7)

The importance of alkyl peroxyl radicals in atmospheric and combustion processes has generated continued interest in the prototypical gas-phase reaction of ethyl radical with dioxygen (reaction 8). The experimental and theoretical data reported thus far have been summarized by Rienstra-Kiracofe et al.,8 who used ab initio electronic structure calculations to investigate mechanisms for the formation of ethylene, acetaldehyde, and oxirane as products of this reaction. All of these channels involve the intermediacy of the ethyl peroxyl radical.

\[ \text{CH}_3\text{CH}_2 + \text{O}_2 \rightarrow [\text{CH}_3\text{CH}_2\text{OO}]^* \] (8)

\[ [\text{CH}_3\text{CH}_2\text{OO}]^* \rightarrow \text{CH}_2 = \text{CH}_2 + \text{OOH} \] (9)

\[ [\text{CH}_3\text{CH}_2\text{OO}]^* \rightarrow \text{CH}_2\text{CHO} + \text{OH} \] (10)

\[ [\text{CH}_3\text{CH}_2\text{OO}]^* \rightarrow \text{c-CH}_2\text{CH}_2\text{O} + \text{OH} \] (11)

If the mechanisms of such reactions can be fully understood, it should be possible to extrapolate them to other, more complex hydrocarbon systems. However, even for this simple model system, crucial issues remain unresolved. In particular, the precise thermochemistry of reaction 8 is still disputed, with theorists5,9 and experimentalists10–13 differing by several kilocalories per mole on the magnitude of the resulting exothermicity.

In this article we describe the measurement of the negative-ion photoelectron spectra of the \(\text{CH}_3\text{OO}^-\), \(\text{CH}_3\text{OO}^-\), and \(\text{CH}_3\text{CH}_2\text{OO}^-\) anions. Analysis of the kinetic energy of the

\[ \text{ROO}^- + h\nu_{364\text{nm}} \rightarrow \text{ROO}^- + e^- \] (KE) (12)

scattered photoelectrons (KE) enables determination of the electron affinity (EA) of the corresponding peroxyl radical, \(\text{EA(ROO)}\). In addition to the photoelectron spectra, we have studied the proton-transfer kinetics of the corresponding hydroperoxides in a tandem flowing afterglow—selected ion flow tube (FA-SIFT). The proton-transfer kinetics establish the gas-phase acidities of the hydroperoxides, \(\Delta_{\text{acid}} \text{G}^{\text{298}}\) (ROO→H). Bond enthalpies of the hydroperoxides \(\Delta_{\text{H}}^{\text{298}}\) (ROO→H) are obtained from the peroxyl radical electron affinities \(\text{[EA(ROO)]}\) and the enthalpy of deprotonation of the corresponding hydroperoxides \(\Delta_{\text{acid}} \text{H}^{\text{298}}\) (ROO→H).

There have been numerous studies of electronic properties of alkyl peroxyl radicals.1,3,8,14 We can use generalized valence bond (GVB) diagrams14–16 to represent the peroxide anions, ROO\(^-\), the peroxyl radicals, ROO, and the peroxyl cations, ROO\(^+\).

\[ \text{ROO}' \quad \text{ROO}^- \quad \text{ROO}'' \quad \text{ROO}''' \quad \text{ROO}'''' \] (14)

\[ \delta^3 X' = 1 \text{eV} \quad \delta^3 X'' = 0 \text{eV} \quad \delta^3 X''' = 1 \text{eV} \quad \delta^3 X'''' = 5 \text{eV} \quad \delta^3 X''''' = 11 \text{eV} \]

The ground electronic state of alkyl peroxyl radicals is ROO\(^-\)\(^{2A''}\). These radicals display two characteristic electronic excited states: a low-lying ROO\(^-\)\(^{2A'}\) state is present at about 1 eV, and there is a high-lying, dissociative state ROO\(^-\) \(^{2\times1}A'\) at a term value of roughly 5 eV. The binding energy14 of the alkyl peroxide anions, ROO\(^-\) \(^{2\times1}A'\), is about 1 eV; ionization energies17 of peroxyl radicals are high \(\text{IP(ROO)} \approx 11 \text{eV}\). The GVB representations depict the HOMO and HOMO-1 of ROO\(^-\) to be localized on the terminal oxygen. Therefore, detachment from these orbitals is expected to excite RO–O stretching modes in forming both the ground state and first excited states of the neutral.

**Experiment**

A. Preparation of Alkyl Hydroperoxides. Methyl hydroperoxide was prepared by methylation of hydrogen peroxide (Fisher Scientific) with dimethyl sulfate (Aldrich) in the presence of potassium hydroxide (Fisher Scientific), according to the literature procedure.18,19 Methyl-d\(_1\) hydroperoxide was prepared in the same way except that dimethyl-d\(_1\) sulfate (Aldrich) was used in place of the unlabeled reagent. Ethyl hydroperoxide was prepared by a procedure analogous to that used for the methyl homologue except diethyl sulfate (Aldrich) was used and a 20-fold increase in reaction time was allowed. tert-Butyl hydroperoxide was obtained as a commercial sample (Aldrich). Care was taken in the preparation and handling of all peroxides, as these are known to be thermally unstable species and explosions have been reported by researchers in other laboratories.18–20

B. Negative-Ion Photoelectron Detachment. The 364 nm photoelectron spectra of \(\text{CH}_3\text{OO}^-\), \(\text{CH}_3\text{OO}^-\), and \(\text{CH}_3\text{CH}_2\text{OO}^-\) were measured with a photoelectron spectrometer that has previously been described in detail.21,22 The anions were prepared by reaction of the parent alkyl hydroperoxide with hydroxide ions in approximately


0.5 Torr of helium in the flowing afterglow ion source. Collisional relaxation with the helium buffer gas served to equilibrate the anions to a vibrational temperature of approximately 300 K. Further cooling to roughly 200 K was achieved by enclosing the flow tube in a jacket of liquid nitrogen. Anions were mass-selected using a Wien velocity filter and subsequently decelerated into an interaction region where the ion beam intersects at right angles with a photon beam from a fixed-frequency (λ0 = 363.8 nm, 3.408 eV) CW argon ion laser in a buildup cavity, yielding approximately 100 W of circulating power. Photoelectrons were collected in a direction perpendicular to the plane of the ion beam—laser interaction and passed through a hemispherical energy analyzer onto a position-sensitive detector. The spectra were recorded as a function of electron kinetic energy (eKE), which is readily converted to electron binding energy (eBE) by subtracting the eKE from the laser photon energy. The absolute energy scale was fixed by the position of the 3P0 → 1P1 transition in the O2 photoelectron spectrum. An additional small (<1%) energy compression factor was applied as determined from the comparison of the photoelectron spectrum of the tungsten ion (W+) with known transitions in tungsten atom.

Given the resolution of the instrument (±0.005 eV or 40 cm⁻¹), rotational bands cannot be resolved. Consequently, the exact peak positions are rotationally uncertain. To assign the exact position of the 00 transition, and thus assign the EA, it is necessary to apply a rotational correction. Let us suppose that the target anions have a mean rotational energy, εrot, where εrot is the Maxwell–Boltzmann average of the ion distribution, εrot = (E'' rot). Consequently, the measured, uncorrected peak position EA is simply

uncorrected EA = EA − εrot + εrot = EA + Δrot(15)

where εrot = (E'' rot) is the Maxwell–Boltzmann average of the neutral distribution. Engelking has derived useful, approximate expressions for the rotational correction, Δrot. In his expressions, k0 is the Boltzmann constant, T is the “effective” temperature of the ion beam, and A, B, and C are the rotational constants of the initial anion (′′ state) and final neutral (′ state). For an asymmetric rotor, he obtains a rotational correction

Δrot = k0 T [A'' 1 B'' 2 + B'' 1 C'' 2 A'' 1 - 3] + (B'' 2 - B'' 1) 3 2 (16)

Using this approach, the rotational corrections applied in this study are ±0.002 eV.

The angular distribution of photoelectrons, I(θ), is given by the expression:

I(θ) = [1 + β(E)P2(cos θ)] (17)

where θ is the angle between the laser electric field vector and the electron collection direction, β is the average photoelectron cross section, P2(cos θ) = 1/2(3 cos² θ − 1), and β(E) is the anisotropy factor that depends on the energy of the photoelectron, E. The polarization of the incident laser beam, θ, can be varied by rotating a half-wave plate in the laser beam path. The photoelectron spectra shown here (Figures 1–3) were collected under conditions where θ was set to the magic angle of 54.7° such that P2(cos θ) = 0 and therefore l(θ) = dθ/4π and is independent of β. Photoelectron spectra were also obtained at the laser polarization angles 0° and 90°. We then determined the asymmetry parameter, β, from the expression

β = [I(θ) - I(90)] [I(θ) + I(90)] (18)

where −1 ≤ β ≤ 2. For molecules, detaching an electron from a π-like orbital yields β < 0, while an electron originating from an α-like orbital gives an angular distribution of photoelectrons with β > 0. In this way, angular distribution information in photoelectron spectra can be used to distinguish between transitions to different electronic states.

Spectra were measured at both 200 and 300 K (room temperature) vibrational temperature and compared in order to identify transitions that originate from vibrationally excited states in the anion. This allows for a secure assignment of the 00 peak.

C. Flowing Afterglow—Selected Ion Flow Tube Measurements.

The gas-phase acidities of CH3OOH, CD3OOH, CH3CH2OOH, and (CH3)2COOH were measured using a tandem flowing afterglow—selected ion flow tube (FA-SIFT) apparatus that has been previously described. The acidity of the parent hydroperoxide was established by measurement of the rate constant for proton transfer between ROOH and a conjugate base of a reference acid, as well as the rate constant for the reverse reaction. Measurements were conducted at 298 K.

ROO− + XH ⇌ ROOH + X− (19)

The ratio of the two measured rate constants, k+ and k−, gives the proton-transfer equilibrium constant Keq(19), which is related to the difference in gas-phase acidities of ROOH and XH by a simple expression. If the acidity of the reference acid is known, Keq(19), then the acidity of the target alkyl peroxide, can be extracted from eq 20.

D. Ab Initio Electronic Structure Calculations. Two different theoretical methods, both of which are available within the GAUSSIAN98 program package,\(^\text{(33)}\) were used to investigate different aspects of the alkyl hydroperoxides. The first approach was the Becke 3LYP hybrid density functional method,\(^\text{(34)}\) employed in conjunction with a correlation-consistent Dunning basis set of double-\(\zeta\) quality (aug-cc-pVDZ)\(^\text{(35)}\) to calculate optimized molecular structures, rotational constants, and harmonic frequencies (these data are available as Supporting Information). Harmonic frequencies and rotational constants calculated using this approach were employed in statistical thermodynamics calculations to derive the entropy and heat capacities of relevant species. The second approach used the Complete Basis Set (CBS)\(^\text{(36,37)}\) method to determine thermodynamic properties of the alkyl hydroperoxides and the alkyl peroxy radicals. The CBS/APNO approach, which has a reported uncertainty of 0.7 kcal mol\(^{-1}\), was adopted for calculation of ROOH and ROO (where \(R = H, \text{CH} \_3, \text{CH} \_2\text{CH} \_3\)). The less demanding

\[
\Delta_{\text{acq}} G_T (\text{ROOH}) - \Delta_{\text{acq}} G_T (\text{HX}) = \Delta\Delta_{\text{acq}} G_T = RT \ln K_{\text{eqi}}(19)
\]

All rate constants reported in this article are presented with their associated statistical uncertainty along with other errors (e.g., mass discrimination and sample contamination). It should be noted that these uncertainties do not include systematic errors due to temperature, flow rates, and pressure measurements. Systematic errors of this kind will be the same for the measurement of forward and reverse rate constants and therefore need not be considered in the determination of \(K_{\text{eqi}}\) and its associated uncertainty. However, the overall uncertainty for any given rate constant will typically be \(\pm 20\%\), where statistical and other errors (e.g., mass discrimination and sample contamination) are smaller than \(20\%\).

The peroxide anions, ROO\(^-\) (where \(R = \text{CH} \_3, \text{CD} \_3, \text{CH} \_2\text{H} \_5\), and \(\text{CH}_3\text{C} \_3\)) were prepared by the reaction of ROOH with a gas-phase base such as hydroxide ion, as previously reported.\(^\text{(29,30)}\) Care was taken to minimize the contact of the alkyl hydroperoxides with metal prior to their introduction into the instrument,\(^\text{(31)}\) and all lines were passivated for several minutes before measurements were undertaken. Reference acids were acetylene (HC≡CH, Matheson) and phenylacetylene (C\(_6\)H\(_5\)C≡CH, Aldrich). These reagents were used without further purification, with the exception of acetylene, which was passed through a stainless steel coil cooled to \(-78\, ^\circ\text{C}\) in a dry ice/acetone bath to remove trace acetone from the sample.\(^\text{(32)}\)


\(^{(34)}\) Becke, A. D. J. Phys. Chem. 1993, 98, 5648.


Transition calculations predict a change in the O bond angle by 5°, and the C–O–O bond angle by 2°. The radical CH₃·OO has a transition 1 0 (O–O stretch), while peaks 1 1 transition, while peaks 2 1 correspond to a progression of six quanta, etc.) to the fundamental 1 0 (CH₃·OO) state, CH₃·OO (see text), and can be fitted to eq 21 using a weighted least-squares approach.

\[ G(v_p) - G(0) = \omega_p (v_p + 1/2) - x_{pp} (v_p + 1/2)^2 - 1/2 \omega_p + 1/4 x_{pp} (21) \]

The extended progression of peaks corresponding to the CH₃·OO X ← CH₃OO− X state transition (Table 1) indicates a significant geometrical change between the ground-state anion and neutral structures. By contrast, the second Franck-Condon envelope of peaks corresponding to the A ← X transition has a narrower profile, with the 0 0 (e1) peak being the most intense and subsequent peaks rapidly decreasing in intensity. This indicates a smaller relative change between the X CH₃OO− and A CH₃O geometries than that observed in the X ← X transition. The anion and neutral structures predicted by both the qualitative GVB expression (eq 14) and B3LYP/aug-cc-pVDZ ab initio calculations support this explanation. In the X ← X transition the O–O bond length is calculated to change by about 0.2 Å and the C–O–O bond angle by 5°. In contrast, the A ← X transition calculations predict a change in the O–O bond length of roughly 0.1 Å and a change in the C–O–O bond angle of about 2° (see Supporting Information).

In the Franck-Condon profile for detachment to the ground state, CH₃OO X ← A, there are two series of features. The most prominent transition is denoted by peaks a1 → a7 in Figure 1. The peak a1 is assigned as the 0 0 transition, while peaks a2 → a7 correspond to a progression of six quanta \((v_p = 1 → 6)\) of an active mode which we label p. The measured energy spacings (Table 1) between the peaks in this progression \((v_p = 1 → 6)\) of mode p and can be fitted to eq 21 using a weighted least-squares approach.

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Fitting these data to eq 21 gives the harmonic frequency of mode \( p \), \( \omega_p = 1147 \pm 3 \text{ cm}^{-1} \), and an anharmonicity term, \( x_p = 12 \pm 1 \text{ cm}^{-1} \). Using these parameters, we can precisely extract a value for the \( 0 \rightarrow 0 \) vibrational transition of mode \( p \), \( \nu_p = 1124 \pm 5 \text{ cm}^{-1} \). In addition to the primary progression, a less intense although clearly resolved second progression is identified in peaks \( b1\text{–}b6 \). These peaks appear to the higher binding energy side of the \( a \) peaks and may be identified as a combination band with this series. We assign \( b1\text{–}b6 \) as a combination of the progression due to mode \( p \), discussed above, plus one quantum of a mode we have labeled \( q \). Taking a weighted average of these energy spacings (Table 2), we obtain the fundamental of mode \( q \) to be \( \nu_q = 482 \pm 9 \text{ cm}^{-1} \).

For the ground state of CD\(_3\)OO, the \( a \) peaks (Table 2) allow us to determine a harmonic frequency, \( \omega_p = 1142 \pm 5 \text{ cm}^{-1} \), and an anharmonicity, \( x_p = 9 \pm 1 \text{ cm}^{-1} \). Using these parameters, we can precisely extract a value for the fundamental of mode \( p \), \( \nu_p = 1123 \pm 7 \text{ cm}^{-1} \). The \( b \) series of peaks is again a combination of the progression due to mode \( p \) plus one quantum of mode \( q \). Taking a weighted average of these energy spacings (Table 2), we obtain the fundamental of mode \( q \) to be \( \nu_q = 440 \pm 7 \text{ cm}^{-1} \).

For ground-state CH\(_3\)OO, the fundamental of the primary progression, \( \nu_p = 1124 \pm 5 \text{ cm}^{-1} \), appears to correlate well with other fundamental O–O vibrational transitions in peroxyl radicals: (i) for HOO, \( \nu_1 = 1097.63 \text{ cm}^{-1} \) as measured by Tuckett and co-workers,\(^{32,43}\) (ii) for matrix-isolated CH\(_2\)OO, \( \nu_5 = 1109 \text{ cm}^{-1} \) measured by Nandi et al.,\(^{44}\) (iii) for CH\(_2\)-OO the ab initio harmonic frequency, \( \omega_b = 1149 \text{ cm}^{-1} \), calculated at the B3LYP/aug-cc-pVDZ level of theory. From both the GVB diagrams (eq 14) and the ab initio geometries, one anticipates strong activity in the RO–O stretching mode upon detachment of the peroxide anion, ROO\(^-\), to the \( X \) state of the neutral. On the basis of these considerations and the good agreement between fundamental frequencies, we assign mode \( p \) to the CH\(_3\)-O stretching mode 6. Similarly, the fundamental frequency \( \nu_p = 482 \pm 9 \text{ cm}^{-1} \) correlates well with both the fundamental \( \nu_p = 492 \text{ cm}^{-1} \) measured by Nandi et al.\(^{44}\) for matrix-isolated CH\(_2\)OO and the harmonic frequency \( \omega_b = 491 \text{ cm}^{-1} \), calculated at the B3LYP/aug-cc-pVDZ level of theory, which corresponds to a H\(_3\)C–O–O bending mode. Theoretical geometries predict activity in the H\(_3\)C–O–O bending mode upon detachment of the peroxide anion, CH\(_2\)OO\(^-\), to the \( X \) state of the neutral radical. These considerations lead us to assign mode \( q \) to the H\(_3\)C–O–O bending mode 8.

These assignments are further supported by the spectrum of CD\(_3\)OO\(^-\). The harmonic (\( \omega_p \)) and fundamental (\( \nu_p \)) frequencies of mode \( p \) extracted from the CD\(_3\)OO\(^-\) spectrum are very similar to those obtained from the CH\(_3\)OO\(^-\) spectrum, and both isotopomers also have similar anharmonicity in this mode. The magnitude of this value is also similar to that observed in the DOO\(^+\) photoelectron spectrum.\(^{38}\) The fact that \( \omega_p \) and fundamental \( \nu_p \) do not change appreciably upon deuteration confirms the assignment of this mode to a localized O–O stretch; a mode that involves hydrogen motion would have been expected to shift to a lower frequency upon deuteration. This rationale is also consistent with the matrix work of Nandi et al., where the fundamental of the O–O stretch mode is largely unaffected by deuteration, shifting from 1109 \pm 12 to 1144 \pm 12 \text{ cm}^{-1} \) in CH\(_2\)OO and CD\(_2\)OO.\(^{44}\) In contrast, the frequency \( \nu_p \) is shifted about 40 \text{ cm}^{-1} \) lower upon deuteration, supporting the assignment of mode \( q \) to the C–O–O bend. Although the hydrogen atoms in this mode may not be moving with respect to the carbon, bending the carbon toward oxygen requires hydrogen motion. Therefore, one would anticipate such a shift to lower frequency. This shift is analogous to that observed in the matrix experiments.\(^{44}\)

Examination of the Franck–Condon envelope for the CH\(_3\)OO \( A \leftarrow \text{CH}_2\text{OO}^- \) \( X \) transition (see expansion Figure 1b) reveals a progression of two active modes of similar intensity. Peak \( c1 \) is assigned to the \( 0_0^0 \) transition, while the peaks \( c2 \) and \( c4 \) correspond to one and two quanta, respectively, of the mode which we designate \( s \). The positions of peaks \( c1 \) and \( c2 \), given in Table 2, fix the fundamental of mode \( s \) to be \( \nu_s = 910 \pm 10 \text{ cm}^{-1} \). The second progression in the excited state is represented by the peaks \( c3 \) and \( c6 \), which correspond to one and two quanta, respectively, of the mode which we have assigned as \( t \). The positions of peaks \( c1 \) and \( c2 \), given in Table 2, fix the fundamental of mode \( t \) to be \( \nu_t = 1005 \pm 10 \text{ cm}^{-1} \). The peak \( c5 \) in Figure 1 represents a combination band of one quantum of \( s \) and one quantum of \( t \).

The \( A \leftarrow X \) transition peaks show activity in two modes (\( s \) and \( t \)) of similar intensity and frequency. The fundamental frequency \( \nu_s = 910 \pm 10 \text{ cm}^{-1} \) is comparable to the frequencies (i) \( \nu_5 = 929.068 \text{ cm}^{-1} \), which is the fundamental of the \( O \rightarrow O \) stretching mode of the \( A \) state of HOO measured by Tuckett and co-workers,\(^{42,43}\) and (ii) the vibrational transition at 896 \pm 9 \text{ cm}^{-1} \) measured for the \( A \) state of CH\(_2\)OO by Hunziker and Wendt.\(^{40}\) The B3LYP/aug-cc-pVDZ calculated harmonic mode \( \omega_s = 917 \text{ cm}^{-1} \) is similar in magnitude to \( \nu_s \) and corresponds to a “symmetric” C–O–O stretching mode. However, the magnitude of \( \nu_s = 1005 \pm 10 \text{ cm}^{-1} \) is not significantly different from that of \( \nu_t \). The former frequency is similar in magnitude to the calculated harmonic frequency \( \omega_t = 1015 \text{ cm}^{-1} \), which corresponds to a C–O–O “antisymmetric” stretching mode. The GVB diagrams and ab initio calculations both predict some activity in the CH\(_3\)O–O stretching vibration for the \( A \leftarrow X \) transition. For this reason, it is not clear which of these two frequencies, if either, could be strictly assigned to an O–O stretch. Furthermore, the ab initio calculations suggest that the \( A \) state vibrations in CH\(_3\)OO are unlike the local modes observed for the ground state, in that the normal modes involve a significant amount of mixing of local modes.

The CD\(_3\)OO\(^-\) spectrum also shows two active modes close in frequency and intensity. One quantum of the first mode is observed at the peak \( c2 \) that appears 840 \text{ cm}^{-1} \) from the \( 0_0^0 \) transition (\( c1 \)), with a second quantum at 1690 \text{ cm}^{-1} (\( c4 \)). The second active mode appears at 975 \text{ cm}^{-1} (\( c3 \)), with a second quantum at 1950 \text{ cm}^{-1} (\( c6 \)). The peak \( c5 \) at 1800 \text{ cm}^{-1} corresponds to a combination band of one quantum of each of these modes. By analogy with the CH\(_3\)OO\(^-\) spectrum, we assign these two modes as \( s \) and \( t \) with fundamentals \( \nu_s = 840 \pm 10 \text{ cm}^{-1} \) and \( \nu_t = 975 \pm 10 \text{ cm}^{-1} \). The value of \( \nu_s \) is red-shifted by about 70 \text{ cm}^{-1} \) compared with the corresponding frequency for CH\(_3\)OO. This indicates a significant hydrogen contribution to the motion of mode \( s \), and therefore this mode cannot be assigned as a pure O–O stretch. By analogy to the \( X \leftarrow X \) state assignments, and by comparison with the ab initio frequency motions discussed for CH\(_3\)OO, there is likely some C–O–O bend involved in the motion. The fundamental frequency \( \nu_t \) has also shifted upon deuteration although somewhat less than in the case of \( \nu_s \). This suggests that H/D motion is a small
component of mode \( t \), and thus it should be closer to a localized O−O stretch than mode \( s \). Thus, we see evidence for mixing between local modes in the two normal modes observed in the \( \tilde{A} \rightarrow \tilde{X} \) transition. On the basis of their intensity, both modes likely have a large component of O−O stretch with contributions from motion involving the hydrogen atoms, likely the C−O−O bend.

The asymmetry parameters \( \beta \) for both electronic transitions in CH\(_3\)OO\(^{-}\) are reported in Table 1. The \( \tilde{X} \rightarrow \tilde{X} \) transition carries an average \( \beta \) of \(-0.7 \pm 0.2\), while the \( \tilde{A} \rightarrow \tilde{X} \) transition has a \( \beta \) of \(-0.2 \pm 0.2\). These values agree well with the corresponding \( \beta \) values observed for HOO.\(^{38}\) They are both negative, suggesting detachment from a \( \pi \)-like orbital. The detachment into the \( \tilde{X} \) state is close to a \( \beta \) of \(-1\), which implies that the detected electrons are ejected from an essentially pure \( \pi \) orbital. Detachment into the \( \tilde{A} \) state yields a \( \beta \) closer to 0, indicating that the orbital from which the electrons are detached possesses some of the \( \sigma \) character of the O−C bond.

**B. Negative-Ion Photoelectron Detachment of CH\(_3\)CH\(_2\)OO\(^{-}\).**

The 200 K magic angle photoelectron spectrum of CH\(_3\)CH\(_2\)OO\(^{-}\) is displayed in Figure 3. The spectrum is more congested than that of CH\(_3\)OO\(^{-}\) or CD\(_3\)OO\(^{-}\), as would be expected for a larger molecule with a greater number of modes. However, the overall structure remains remarkably similar. One sees the same peak intensity envelopes representing transitions into two electronic states of the neutral. The peak \( c1 \) is assigned to the \( 0^0 \) feature of the \( \tilde{A} \rightarrow \tilde{X} \) transition. Peak \( a1 \) is the origin of the \( \tilde{X} \rightarrow \tilde{X} \) transition and thus gives the electron affinity, \( E_{\text{A}}(\text{CH}_3\text{CH}_2\text{OO}) = 1.186 \pm 0.004 \) eV, and the term energy, \( \Theta_0 = 0.938 \pm 0.004 \) eV (7565 \( \pm \) 30 cm\(^{-1}\)), in agreement with the earlier findings of Hunziker and Wendt (7593 \( \pm \) 6 cm\(^{-1}\)).\(^{40}\) The same primary ground-state progression observed in CH\(_3\)OO\(^{-}\) and CD\(_3\)OO\(^{-}\) appears in peaks \( a1 \rightarrow a5 \), and we assign the active mode responsible as \( p \). Fitting the energy spacings (Table 3) to eq 21 as previously described gives the harmonic frequency, \( \omega_p = 1096 \pm 10 \) cm\(^{-1}\), and a small anharmonicity, \( \chi_{pp} = 4 \pm 2 \) cm\(^{-1}\). Using these parameters, we can extract the fundamental frequency of mode \( p \) to be \( \nu_p = 1089 \pm 16 \) cm\(^{-1}\). A second progression, \( b1 \rightarrow b6 \), is assigned as a combination of the progression due to mode \( p \) plus one quantum of a mode we have labeled \( u \). Taking a weighted average of these energy spacings (Table 3), we obtain the fundamental of mode \( u \) to be \( \nu_u = 234 \pm 9 \) cm\(^{-1}\). This frequency is small enough that one would expect to observe a combination band involving two quanta of mode \( u \) on top of the \( p \) progression. This is supported by the observation of peak \( bb4 \); however, any other members of such a progression are obscured by noise in the data.

The similarity of \( \omega_p \) and \( \nu_p \) between CH\(_3\)OO, CD\(_3\)OO, and CH\(_3\)CH\(_2\)OO\(^{-}\) is evidence that this frequency corresponds to a local O−O stretching mode, as increasing the mass of the alkyl substituent has a minimal effect on the measured frequency. The fundamental frequency, \( \nu_p = 1089 \pm 10 \) cm\(^{-1}\), for CH\(_3\)CH\(_2\)OO also correlates well with the O−O stretching frequencies: (i) \( \nu_1 = 1097.6 \) cm\(^{-1}\) measured\(^{42,43}\) for HOO, (ii) \( \nu_2 = 1112 \) cm\(^{-1}\) measured\(^{45}\) for matrix-isolated CH\(_3\)CH\(_2\)OO, and (iii) \( \omega_3 = 1199 \) cm\(^{-1}\), the calculated harmonic frequency that corresponds to a localized O−O stretching mode. On the basis of these considerations, we assign mode \( p \) to the CH\(_3\)CH\(_2\)O−O stretching mode 8.

The assignment of mode \( u \) is not assisted by matrix frequency data, as they cannot observe such low frequencies. However, analogy with the CH\(_3\)OO and CD\(_3\)OO radicals would identify \( u \) as a bending mode. Furthermore, the downward shift in the

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<table>
<thead>
<tr>
<th>Table 3. Negative-Ion Photoelectron Peak Positions (rotationally uncorrected) for CH(_3)CH(_2)OO(^{-})</th>
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<tbody>
<tr>
<td>CH(_3)CH(_2)OO(^{-}) + h(\nu) (\rightarrow) CH(_3)CH(_2)OO + e(^{-}) (KE)</td>
</tr>
<tr>
<td>for CH(_3)CH(_2)OO the fundamentals are:</td>
</tr>
<tr>
<td>( \nu_a = 234(9) ) cm(^{-1}) (bend),</td>
</tr>
<tr>
<td>( \nu_s = 900(15) ) cm(^{-1}) (O−O stretch),</td>
</tr>
<tr>
<td>( \nu_v = 178(10) ) cm(^{-1}) (bend)</td>
</tr>
<tr>
<td>( \tilde{X} 2\text{A}'' )</td>
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<tr>
<td>( a1 ) ( \nu'_0 ) ( \nu''_0 )</td>
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<tr>
<td>( b1 ) ( \nu'_1 ) ( \nu''_1 )</td>
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<tr>
<td>( a2 ) ( \nu'_2 )</td>
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<tr>
<td>( b2 ) ( \nu'_1 \nu'_2 ) ( \nu''_1 \nu''_2 )</td>
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<tr>
<td>( a3 ) ( \nu'_3 )</td>
</tr>
<tr>
<td>( b3 ) ( \nu'_1 \nu'_2 \nu'_3 ) ( \nu''_1 \nu''_2 \nu''_3 )</td>
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<tr>
<td>( a4 ) ( \nu'_4 )</td>
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<tr>
<td>( b4 ) ( \nu'_1 \nu'_2 \nu'_3 \nu'_4 ) ( \nu''_1 \nu''_2 \nu''_3 \nu''_4 )</td>
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<tr>
<td>( bb4 ) ( \nu'_1 \nu'_2 \nu'_3 \nu'_4 ) ( \nu''_1 \nu''_2 \nu''_3 \nu''_4 )</td>
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<tr>
<td>( a5 ) ( \nu'_5 )</td>
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<tr>
<td>( b5 ) ( \nu'_1 \nu'_2 \nu'_3 \nu'_4 \nu'_5 ) ( \nu''_1 \nu''_2 \nu''_3 \nu''_4 \nu''_5 )</td>
</tr>
<tr>
<td>( a6 ) ( \nu'_6 )</td>
</tr>
<tr>
<td>( b6 ) ( \nu'_1 \nu'_2 \nu'_3 \nu'_4 \nu'_5 \nu'_6 ) ( \nu''_1 \nu''_2 \nu''_3 \nu''_4 \nu''_5 \nu''_6 )</td>
</tr>
<tr>
<td>( a7 ) ( \nu'_7 )</td>
</tr>
<tr>
<td>( \tilde{A} 2\text{A}' ) ( \nu' ) ( \nu'' )</td>
</tr>
<tr>
<td>( c1 ) ( \nu'_0 ) ( \nu''_0 )</td>
</tr>
<tr>
<td>( d1 ) ( \nu'_1 \nu''_1 )</td>
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<tr>
<td>( c2 ) ( \nu'_2 \nu''_2 )</td>
</tr>
<tr>
<td>( d2 ) ( \nu'_1 \nu'_2 \nu''_1 \nu''_2 )</td>
</tr>
<tr>
<td>( c3 ) ( \nu'_3 \nu''_3 )</td>
</tr>
<tr>
<td>( d3 ) ( \nu'_1 \nu'_2 \nu'_3 \nu''_1 \nu''_2 \nu''_3 )</td>
</tr>
</tbody>
</table>

*Peak positions are given in wavenumbers (cm\(^{-1}\)) relative to \( 0^0 \) transitions (peaks \( a1 \) and \( c1 \)). Assignments are given for the most prominent transitions labeled as indicated in Figure 3. See text for details.*

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CH₃OO and CD₃OO, the second series of peaks corresponds to an active mode with a small fundamental frequency, νᵣ = 178 ± 10 cm⁻¹. Thus, mode ν is not expected to involve any significant O=O stretching character. The low frequency is more consistent with a bending motion. The lowest calculated harmonic frequency of α symmetry is 0₁₃ = 279 cm⁻¹, which corresponds to a C=O=O bending mode.

The β parameters for the two CH₃CH₂OO⁻ electronic transitions are given in Table 1. The X ← X' and the A ← X transitions have the same asymmetry, with a negative value of −0.2 ± 0.2. This finding is consistent with the other peroxide systems studied, where negative β parameters are also observed for both transitions.¹⁴

C. Gas-Phase Acidity. Acetylene (ΔacidG₂₉₈[C₂H₂] = 370.3 ± 0.3 kcal mol⁻¹) was used as a reference acid to establish the gas-phase acidities of methyl and methyl-d₃ hydroperoxides, by measuring the proton-transfer kinetics.

CH₃OO⁻ + HC≡CH ⇌ CH₂OOH + HC≡C⁻ (22)

CD₃OO⁻ + HC≡CH ⇌ CD₂OOH + HC≡C⁻ (23)

The reaction of the methyl peroxide anion with acetylene was found to give two product ions: (i) the acetylide ion, generated by proton transfer, and (ii) the CH₃OO⁻−C₂H₂ cluster ion. The overall reaction rate constant, koverall = 2.09 ± 0.13 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹, represents the measured rate of depletion of the reactant anion. This value is small, suggesting a slow, endothermic reaction. In such cases, the cluster is usually thought to form from ions in the low-energy fraction of the thermal ion population, while the higher energy fraction undergoes the proton transfer. Therefore, the overall rate (koverall) is multiplied by the amount of proton-transfer product ions as a fraction of all product ions to give the rate of proton transfer, k₂₃ = 1.25 ± 0.38 × 10⁻¹¹ cm³ molecule⁻¹ s⁻¹. The stated uncertainty for this rate also takes into account mass discrimination effects involved in such a treatment. The reverse reaction of the acetylide ion with methyl hydroperoxide was found to proceed significantly more rapidly and to form no clusters. The exothermic reaction produces two major product ions: (i) the methyl peroxide anion was generated by proton transfer and (ii) the hydroxide anion was produced via an E₀2 mechanism similar to that described by DePay and co-workers for methyl nitrite (eq 24).⁴⁹,⁵⁰

CH₃OOH + HC≡C⁻ → CH₂O + HO⁻ + HC≡CH (24)

Electronic structure calculations show that these two reactions both proceed energetically below the entrance channel and may therefore be considered as directly competitive.⁵⁰ Thus, the overall uncorrected rate constant for acetylide ion depletion may be used for the rate of proton transfer, k₂₃ = 5.62 ± 0.15 × 10⁻¹² cm³ molecule⁻¹ s⁻¹. However, the methyl hydroperoxide was contaminated with some diethyl ether resulting from incomplete separation during the synthetic preparation. Although diethyl ether does not react with acetylide,⁵¹ it may decrease the measured concentration of methyl hydroperoxide and consequently give an artificially lower reaction rate. As a consequence, we used the measured rate constant as a lower limit for the true rate of proton transfer and utilized the calculated collision rate, kcollision = 3.0 × 10⁻⁷ cm³ molecule⁻¹ s⁻¹, as an upper limit for this exothermic proton transfer. Combining these boundary rates with k₂₃, according to eq 20, gives a recommended value of ΔacidG₂₉₈ = −2.7 ± 0.6 kcal mol⁻¹, where the stated uncertainty includes both upper and lower bounds. Thus, the absolute gas-phase acidity of methyl hydroperoxide is ΔacidG₂₉₈[CH₃OOH] = 367.6 ± 0.7 kcal mol⁻¹.

Despite the conservative assignments of error limits, the final uncertainty for the gas-phase acidity is still pleasingly small.⁵³ An analogous treatment of the data for methyl-d₃ hydroperoxide gave the following rates for forward and reverse proton-transfer reactions: k₂₃ = 1.43 ± 0.45 × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ and k⁻₂₃ = 2.65 ± (0.07) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ (kcollision = 2.28 × 10⁻⁹ cm³ molecule⁻¹ s⁻¹). Using these results, we recommend a value of ΔacidG₂₉₈ = −2.4 ± 0.8 kcal mol⁻¹, and thus the absolute gas-phase acidity is determined to be ΔacidG₂₉₈[CD₃OOH] = 367.9 ± 0.9 kcal mol⁻¹.

We used phenyl acetylene (ΔacidG₂₉₈[C₆H₅CH≡CH] = 362.9 ± 0.2 kcal mol⁻¹)⁵₄ as a reference acid to establish the gas-phase acidity of ethyl hydroperoxide. Although the gas-phase acidity of hydrogen fluoride (ΔacidG₂₉₈[HF] = 365.8 ± 0.2 kcal mol⁻¹) is more precisely known,⁵⁵–⁵⁹ reactions of HF with CH₃CH₂OO⁻ and F⁻ with CH₃CH₂OOH led to numerous reaction channels which obscured the proton-transfer kinetics.⁵⁰

CH₃CH₂OO⁻ + C₆H₅C≡CH ⇌ CH₂CH₂OOH + C₆H₅C≡C⁻ (25)

The reaction of the ethyl peroxide anion with phenyl acetylene produces the phenyl acetylide anion exclusively. This proton transfer is rapid, with a rate constant of k₂₃ = 1.18 ± (0.06) × 10⁻⁹ cm³ molecule⁻¹ s⁻¹, suggesting an exothermic reaction. The reverse reaction of the phenyl acetylide anion with ethyl hydroperoxide produced (i) the ethyl peroxide anion by proton

(⁵¹) No ethoxide ions (CH₃CH₂O⁻) were detected in this reaction, suggesting that diethyl ether does not react with the acetylide ions under these conditions.


(⁵³) A reviewer has expressed some concern regarding our method for deriving the forward rate constant for proton transfer (k₂₃). In our treatment, the cluster ions are excluded from the overall measured rate constant (koverall) in order to derive the rate of the proton transfer. Although we believe this logic is sound, if we include the cluster ions and use simply the koverall for the rate of proton transfer, we calculate ΔacidG₂₉₈ = −2.4 ± 0.4 kcal mol⁻¹, which falls almost entirely within the stated uncertainty of our recommended value.


(⁵⁵) The ΔacidG₂₉₈ value for HF can be calculated from the known heats of formation and entropies of HF, H⁺, and F⁻ that are given here and are reported in the references indicated: ΔacidG₂₉₈[HF] = −65.320 ± 0.167 kcal mol⁻¹, ΔacidG₂₉₈[HF] = 41.5342 ± 0.0007 cal mol⁻¹ K⁻¹, ΔacidG₂₉₈[H⁺] = −59.456 ± 0.072 kcal mol⁻¹, ΔacidG₂₉₈[F⁻] = 34.794 ± 0.009 cal mol⁻¹ K⁻¹, ΔacidG₂₉₈[F⁻] = 365.6828 ± 0.0025 kcal mol⁻¹, ΔacidG₂₉₈[H⁺] = 26.040 ± 0.009 cal mol⁻¹ K⁻¹.


transfer and the secondary cluster ions, CH₃CH₅OO⁻−(CH₃CH₂OOH) and CH₃CH₅OO⁻−(CH₃CH₂OOH)₂, and (ii) the hydroxide and acetaldehyde enolate anions by the EC₄O₂ mechanism previously discussed (cf. eq 24). The overall rate coefficient, kₕoverall, is 4.20 (±0.12) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, is significantly smaller than that of the forward reaction, demonstrating that the reverse proton transfer is endothermic.

For a slow endothermic reaction, it is unclear whether (i) the proton-transfer and EC₄O₂ reactions are directly competitive (cf. k₋₂) or (ii) the proton-transfer and EC₄O₂ reactions arise from different energy fractions of the thermal ion population. Thus, there are two possible treatments of these data: (i) the overall reaction rate, kₕoverall, is taken to represent the proton-transfer rate k₋₂, giving ΔΔₕacidG₂⁹₈ = 0.61 ± 0.03 kcal mol⁻¹, or (ii) the overall rate is partitioned, based on the fraction of proton-transfer product ions, giving k₋₂ = 1.77 (±0.88) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹, where the large uncertainty is due to mass discrimination effects. This gives ΔΔₕacidG₂⁹₈ = 1.1 ± 0.3 kcal mol⁻¹.

For such an endothermic reaction, neither scenario may be discounted, and we therefore recommend a difference in gas-phase acidities of ΔΔₕacidG₂⁹₈ = 1.0 ± 0.4 kcal mol⁻¹ to cover both possibilities. This gives a conservative gas-phase acidity of ΔΔₕacidG₂⁹₈(CH₃CH₂OOH) = 363.9 ± 2.0 kcal mol⁻¹. It is significant to note that the uncertainty due to the treatment of k₋₂ is almost completely absorbed by the large uncertainty in the gas-phase acidity of the reference acid, phenyl acetylene (ΔΔₕacidG₂⁹₈[CH₆H₅C≡C] = 362.9 ± 2.0 kcal mol⁻¹).

To make meaningful thermochemical comparisons between alkyl peroxides, the rates of proton transfer were measured under the same conditions for tert-buty1 hydroperoxide with phenyl acetylene. In the absence of α-hydrogens on the tert-buty1 hydroperoxide, the forward and reverse rate constants were only corrected for clustering reactions that are particularly prevalent for such a large system.

\[(CH₃)₃COO⁻ + C₆H₅C≡C\ → \ (CH₃)₃COOH + C₆H₅C≡C⁻ \]  (26)

These corrections yield the rates k₋₂ = 7.29 (±1.46) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ and k₋₂ = 7.54 (±1.51) × 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹. The similarity between the rates suggests a nearly thermonutral reaction with ΔΔₕacidG₂⁹₈ = -0.02 ± 0.17 kcal mol⁻¹, such that ΔΔₕacidG₂⁹₈[(CH₃)₃COOH] = 362.9 ± 2.0 kcal mol⁻¹, in good agreement with the previously reported value of ΔΔₕacidG₂⁹₈[(CH₃)₃COOH] = 363.2 ± 2.0 kcal mol⁻¹ (we recommend the revised value for future reference). It is important, however, that this experiment fixes the difference in gas-phase acidity between ethyl and tert-buty1 hydroperoxide to be 1.0 ± 0.4 kcal mol⁻¹.

D. Entropy and Enthalpy Calculations. One can extract bond energies from measured electron affinities and gas-phase acidities. Simple thermochemical cycle in eq 27 combines (i) the enthalpy of deprotonation of the parent alkyl hydroperoxide (ΔΔₕacidH₂⁹₈[ROOH]) with (ii) the electron affinity of the corresponding alkyl peroxyl radical (EA[ROO⁺]) and (iii) the ionization potential of the hydrogen atom (IP[H]), yielding the ROO−H bond dissociation enthalpy (DH₂⁹₈[ROO−H]) for the alkyl hydroperoxide.

The final term in this expression corresponds to the sum of the integrated heat capacities, which is always small (≤0.3 kcal mol⁻¹) and can therefore be ignored in favor of the simplified expression

\[DH₂⁹₈[ROO−H] = \DeltaΔₕacidH₂⁹₈[ROOH] − IP[H] + EA[ROO] \]

\[\int_0^{298} dT(C_p[ROO] − C_p[ROO⁺] + C_p[H] − C_p[H⁺]) \]  (27)

\[DH₂⁹₈[ROO−H] ≈ \DeltaΔₕacidH₂⁹₈[ROOH] − IP[H] + EA[ROO] \]  (28)

The ΔΔₕacidH₂⁹₈[ROOH] term in eq 28 must be extracted from the experimentally determined ΔΔₕacidG₂⁹₈ value and a calculated entropy of deprotonation, ΔΔₕacidH₂⁹₈, via the simple relation ΔΔₕacidH₂⁹₈ = ΔΔₕacidG₂⁹₈ + TΔΔₕs₂⁹₈. Ab initio electronic structure calculations (Becke 3LYP hybrid density functional calculations) were employed to generate harmonic vibrational frequencies and rotational constants for the ROOH and ROO− species. These values are tabulated as Supporting Information and were used to estimate the entropies of these molecules using equilibrium statistical thermodynamics, with rigid rotor and harmonic oscillator approximations. Clearly, when R = CH₃, CH₂CH₃, and (CH₃)₂C, both ROOH and ROO− species will possess low-energy internal rotors. For the most part, however, the contributions of the internal rotors to the entropy will be common to both ROOH and ROO− and will therefore cancel out in the calculation of ΔΔₕs₂⁹₈. The exception to this is the internal rotation about the RO−OH axis in the alkyl hydroperoxides. In the absence of experimental rotational data for these species, a more rigorous treatment of the entropy to include an explicit treatment of the contributions of the RO−OH rotor would also include some approximations. To allow for these problems involving internal rotors, we chose the very conservative uncertainty limits of ±2.3 cal mol⁻¹ K⁻¹ for our calculated ΔΔₕs₂⁹₈ values. The following entropies of deprotonation were computed: ΔΔₕacidH₂⁹₈[CH₃OOH] = 23.3 ± 2.3 cal mol⁻¹ K⁻¹, ΔΔₕacidH₂⁹₈[CD₃OOH] = 23.3 ± 2.3 cal mol⁻¹ K⁻¹, ΔΔₕacidH₂⁹₈[CH₃CH₂OOH] = 23.8 ± 2.3 cal mol⁻¹ K⁻¹, and ΔΔₕacidH₂⁹₈[[(CH₃)₃C]OOH] = 24.5 ± 2.3 cal mol⁻¹ K⁻¹. Use of these calculated entropies with the measured acidities provides the enthalpies of deprotonation: ΔΔₕacidH₂⁹₈[CH₃OOH] = 374.6 ± 1.0 kcal mol⁻¹, ΔΔₕacidH₂⁹₈[CD₃OOH] = 374.9 ± 1.1 kcal mol⁻¹, ΔΔₕacidH₂⁹₈[CH₃CH₂OOH] = 371.0 ± 2.2 kcal mol⁻¹, and ΔΔₕacidH₂⁹₈[[(CH₃)₃C]OOH] = 370.2 ± 2.1 kcal mol⁻¹. Using the measured electron affinities of EA[CH₃OO] = 26.8 ± 0.1 kcal mol⁻¹, EA[CD₃OO] = 26.6 ± 0.1 kcal mol⁻¹, EA[CH₃CH₂OO] = 27.3 ± 0.1 kcal mol⁻¹, and EA[[(CH₃)₃C]OO] = 27.6 ± 0.3 kcal mol⁻¹ the precisely known ionization potential of the hydrogen atom, ΔΔₕH₂⁹₈[H] = 313.587 347 ± 0.000 001 kcal mol⁻¹, the bond dissociation enthalpies are calculated, via eq 28, to be DH₂⁹₈[CH₃OO−H] = 87.8 ± 1.0 kcal mol⁻¹, DH₂⁹₈[CD₃OO−H] = 87.9 ± 1.1 kcal mol⁻¹, DH₂⁹₈[CH₃CH₂OO−H] = 84.8 ± 2.2 kcal mol⁻¹, and DH₂⁹₈[[(CH₃)₃C]OO−H] = 84.2 ± 2.1 kcal mol⁻¹. By making a small correction for the difference in heat capacities at 298 K (see eq (64) Hodgson, D. W.; McKinnon, J. T., manuscript in preparation, 2001.


(63) The potential problems arising from internal rotor contributions to ΔΔₕs₂⁹₈. We checked our harmonic oscillator–rigid rotor ΔΔₕs₂⁹₈ values against those calculated using the software package of Hodgson and McKinnon. The latter approach separates Sₕ from Srot and calculates each explicitly. This calculation gives ΔΔₕs₂⁹₈(CH₃OOH) = 23.0 kcal mol⁻¹ K⁻¹ and ΔΔₕs₂⁹₈(CH₃CH₂OOH) = 23.6 kcal mol⁻¹ K⁻¹, which differ from our harmonic oscillator–rigid rotor values (Table 4) by <0.5 kcal mol⁻¹ K⁻¹, which is within the stated uncertainty.


29), it is possible to calculate the bond enthalpy at the 0 K limit which is, by definition, the bond dissociation energy.50,66

\[ D_0[\text{ROO} - \text{H}] = DH_{298}[\text{ROO} - \text{H}] - \int_0^{298} d\ell(C_p[\text{ROO}] - C_p[\text{ROOH}] + C_p[\text{H}]) \]  

(29)

The heat capacities \( C_p[\text{ROOH}], C_p[\text{ROO}], \) and \( C_p[\text{H}] \) can be estimated\(^6,62\) using calculated data. Such calculations give \( D_0[\text{CH}_3\text{OO} - \text{H}] = 86.9 \pm 1.0 \) kcal mol\(^{-1}\), \( D_0[\text{CD} \_3 \text{OO} - \text{H}] = 87.0 \pm 1.1 \) kcal mol\(^{-1}\), \( D_0[\text{CH}_3\text{CH}_2\text{OO} - \text{H}] = 83.9 \pm 2.2 \) kcal mol\(^{-1}\), and \( D_0[(\text{CH}_3)_2\text{COOH} - \text{H}] = 83.3 \pm 2.1 \) kcal mol\(^{-1}\).

### Discussion

#### A. Thermochemistry

The thermochemical parameters that have been determined in this study for \( \text{CH}_3\text{OO} \) and \( \text{CH}_3\text{CH}_2\text{OO} \) and the corresponding hydroperoxides are listed in Table 4. These data are augmented with values previously measured for the \( \text{HOO} \) and \( (\text{CH}_3)_2\text{COO} \) radicals. Bond enthalpies calculated using Complete Basis Set\(^{36,37}\) ab initio electronic structure methods appear as a footnote to Table 4. The experimentally derived bond enthalpies, \( DH_{298}[\text{ROO} - \text{H}] \), presented above give rise to the possibility of determining accurate heats of formation for the corresponding peroxyl radicals, \( \Delta H_{298}[\text{ROO}] \), by the simple relationship:

\[ \Delta H_{298}[\text{ROO}] = DH_{298}[\text{ROO} - \text{H}] + \Delta H_{298}[\text{ROOH}] - \Delta H_{298}[\text{H}] \]  

(30)

However, to extract the heat of formation of the ROO radical in this way, the heat of formation of the parent hydroperoxide, \( \Delta H_{298}[\text{ROOH}] \), is required. The available literature values are collected in Table 5, but selecting a single reliable heat of formation for either \( \text{CH}_3\text{OOH} \) or \( \text{CH}_3\text{CH}_2\text{OOH} \) proves difficult, as neither has been precisely measured. Two problems are identified that make these compounds difficult to study experimentally: (i) the difficulty in obtaining pure compounds, and (ii) the instability of these small alkyl hydroperoxides, which have a susceptibility to heterogeneous decomposition on metal and glass surfaces.\(^5\)

The only experiment data in the literature\(^68,69\) appear to be \( \Delta H_{298}[\text{CH}_3\text{OOH}] = -31.3 \) kcal mol\(^{-1}\) (for which no uncertainty is specified) and \( \Delta H_{298}[\text{CH}_3\text{CH}_2\text{OOH}] = -45 \pm 12 \) kcal mol\(^{-1}\). The earliest estimates in the literature are those derived by Benson and co-workers\(^67,70\) utilizing the group additivity (GA) scheme,\(^71,72\) based on the experimentally measured heats of formation for the dialkyl peroxides and hydrogen peroxide. The most recent group additivity values give \( \Delta H_{298}[\text{CH}_3\text{OOH}] = -31.4 \pm 1.0 \) kcal mol\(^{-1}\) and \( \Delta H_{298}[\text{CH}_3\text{CH}_2\text{OOH}] = -39.4 \pm 1.0 \) kcal mol\(^{-1}\), where the confidence limits are estimated by comparing GA values with the experimental data\(^73\) available for \( \text{HOOH} \) and \( (\text{CH}_3)_2\text{COOH} \)

<table>
<thead>
<tr>
<th>HOO</th>
<th>CH$_3$OO</th>
<th>CH$_3$HOO</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.160 ± 0.005 kcal mol$^{-1}$</td>
<td>1.186 ± 0.004 kcal mol$^{-1}$</td>
<td>1.196 ± 0.011 kcal mol$^{-1}$</td>
</tr>
</tbody>
</table>

**Table 4.** Thermochemical Parameters Determined for the Peroxyl Radicals HOO and Their Corresponding Hydroperoxide Species ROOH, where R = H, CH$_3$, CD$_3$, CH$_2$H, and (CH$_3$)$_2$C

CBS-APNO calculations give the following bond enthalpies for comparison with our experimental values: \( DH_{298}[\text{HOO} - \text{H}] = 86.7 \pm 0.7 \) kcal mol$^{-1}$, \( DH_{298}[\text{CH}_3\text{OO} - \text{H}] = 85.1 \pm 0.7 \) kcal mol$^{-1}$, and \( DH_{298}[\text{CH}_3\text{CH}_2\text{OO} - \text{H}] = 84.9 \pm 0.7 \) kcal mol$^{-1}$. CBS-Q calculations give \( DH_{298}[\text{H}_2\text{COOH} - \text{H}] = 83.6 \pm 1.2 \) kcal mol$^{-1}$. (Table 5). Benassi et al. have calculated the heats of formation using molecular mechanics and low-level ab initio methods.\(^74\)

Employing an atom equivalents scheme, they recommend the values \( \Delta H_{298}[\text{CH}_3\text{OOH}] = -33 \) kcal mol$^{-1}$ and \( \Delta H_{298}[\text{CH}_2\text{CH}_2\text{OOH}] = -40 \) kcal mol$^{-1}$. Lay et al. have attempted to evaluate the available thermodynamic data to obtain a best estimate for the heat of formation of methyl hydroperoxide.\(^75\)

They use the heat of formation of methyl peroxyl radical determined by Slagle and Gutman\(^10\) from experimental data and an estimated “average bond energy” for the O–H bond in ROOH compounds of \( 88.2 \pm 0.4 \) kcal mol$^{-1}$ to derive \( \Delta H_{298}[\text{CH}_3\text{OOH}] = -33.4 \pm 1.2 \) kcal mol$^{-1}$. This value is combined with data from isodesmic reaction calculations to give a computed value for the heat of formation of ethyl hydroper-
Table 5. Comparison of the Available Literature Heats of Formation (kcal mol⁻¹) for ROO and ROOH with Those Determined in This Study, where R = H, CH₃, CH₂CH₃, (CH₃)₂C

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔH₂⁹⁸/Kcal mol⁻¹</th>
<th>Source/Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔH₂⁹⁸[HOO]</td>
<td>3.0 ± 0.4</td>
<td>OH + CIo ↔ HOO + Cl⁺⁺</td>
</tr>
<tr>
<td></td>
<td>3.3 ± 0.8</td>
<td>IE(HOO) and AE(HOO⁺/HOOH)</td>
</tr>
<tr>
<td></td>
<td>3.5 ± 0.5</td>
<td>group additivity</td>
</tr>
<tr>
<td></td>
<td>2.9 ± 0.7</td>
<td>CBS/APNO calculation</td>
</tr>
<tr>
<td></td>
<td>3.3 ± 0.9</td>
<td>negative-ion/acidity/CBS</td>
</tr>
<tr>
<td>ΔH₂⁹⁸[HOOH]</td>
<td>−32.48 ± 0.05</td>
<td>calorimetry</td>
</tr>
<tr>
<td></td>
<td>−32.5 ± 1.0</td>
<td>group additivity</td>
</tr>
<tr>
<td></td>
<td>−31.7 ± 0.7</td>
<td>CBS/APNO calculation</td>
</tr>
<tr>
<td>ΔH₂⁹⁸[CH₃OO]</td>
<td>2.7 ± 0.8</td>
<td>CH₃ + O₂ ↔ CH₃OO</td>
</tr>
<tr>
<td></td>
<td>2.9 ± 1.5</td>
<td>CH₃ + O₂ ↔ CH₃OO</td>
</tr>
<tr>
<td></td>
<td>2.2 ± 1.2</td>
<td>CH₃ + O₂ ↔ CH₃OO</td>
</tr>
<tr>
<td></td>
<td>5.5 ± 1.0</td>
<td>Br + CH₃OH ↔ CH₃OO + HBr⁺⁺ tied to DH₀[CH₃OO−H] = 88.5 ± 0.5 kcal mol⁻¹ and ΔH₂⁹⁸[CH₃OOH] = 30.9 ± 1.0 kcal mol⁻¹</td>
</tr>
<tr>
<td></td>
<td>5.2 ± 1.1</td>
<td>group additivity</td>
</tr>
<tr>
<td></td>
<td>2.07 ± 0.7</td>
<td>CBS/APNO</td>
</tr>
<tr>
<td></td>
<td>4.8 ± 1.2</td>
<td>negative-ion/acidity/CBS</td>
</tr>
<tr>
<td>ΔH₂⁹⁸[CH₃OOH]</td>
<td>−33 ± 3.6</td>
<td>MM and ab initio calculation</td>
</tr>
<tr>
<td></td>
<td>−33.4 ± 1.2</td>
<td>ΔH₂⁹⁸[CH₃OOH]¹⁰ and estimated DH₂⁹⁸[CH₃OO−H]⁷⁵</td>
</tr>
<tr>
<td></td>
<td>−31.3 ± 0.6</td>
<td>heat of equilibrium measurement³⁸</td>
</tr>
<tr>
<td></td>
<td>−31.4 ± 1.0</td>
<td>group additivity</td>
</tr>
<tr>
<td></td>
<td>−30.9 ± 0.7</td>
<td>CBS/APNO</td>
</tr>
<tr>
<td>ΔH₂⁹⁸[CH₂CH₂OO]</td>
<td>−6.5 ± 2.4</td>
<td>CH₂CH₃ + O₂ ↔ CH₂CH₂OO</td>
</tr>
<tr>
<td></td>
<td>−2.9 ± 1.1</td>
<td>group additivity</td>
</tr>
<tr>
<td></td>
<td>−6.8 ± 0.7</td>
<td>CBS/APNO</td>
</tr>
<tr>
<td></td>
<td>−6.8 ± 2.3</td>
<td>negative-ion/acidity/CBS</td>
</tr>
<tr>
<td>ΔH₂⁹⁸[CH₂CH₂OOH]</td>
<td>−45 ± 12</td>
<td>static bomb calorimetry</td>
</tr>
<tr>
<td></td>
<td>−40 ± 5.0</td>
<td>MM and ab initio calculation</td>
</tr>
<tr>
<td></td>
<td>−41.5 ± 1.5</td>
<td>calculation of isodesmic reactions⁷⁵</td>
</tr>
<tr>
<td></td>
<td>−39.4 ± 1.0</td>
<td>group additivity</td>
</tr>
<tr>
<td></td>
<td>−39.5 ± 0.7</td>
<td>CBS/APNO</td>
</tr>
<tr>
<td>ΔH₂⁹⁸[(CH₃)₂COO]</td>
<td>−20.7 ± 0.8</td>
<td>Br + [(CH₃)₂COO] ↔ [(CH₃)₂COO] + HBr⁺⁺</td>
</tr>
<tr>
<td></td>
<td>−24.3 ± 2.2</td>
<td>(CH₃)C + O₂ ↔ (CH₃)COO</td>
</tr>
<tr>
<td></td>
<td>−21.4 ± 1.1</td>
<td>group additivity</td>
</tr>
<tr>
<td></td>
<td>−25.8 ± 1.2</td>
<td>CBS-Q</td>
</tr>
<tr>
<td></td>
<td>−25.2 ± 2.5</td>
<td>negative-ion/acidity/CBS</td>
</tr>
<tr>
<td>ΔH₂⁹⁸[(CH₃)₂COOH]</td>
<td>−58.8 ± 12</td>
<td>calorimetry</td>
</tr>
<tr>
<td></td>
<td>−56.1 ± 0.6</td>
<td>heat of equilibrium measurement³⁸</td>
</tr>
<tr>
<td></td>
<td>−57.9 ± 1.0</td>
<td>group additivity</td>
</tr>
<tr>
<td></td>
<td>−57.3 ± 1.2</td>
<td>CBS-Q</td>
</tr>
</tbody>
</table>

Note: The uncertainties are ±0.7 and 1.2 kcal mol⁻¹ for CBS/APNO and CBS-Q, respectively. The values shown are the experimental bond enthalpies from CBS/APNO or CBS-Q calculation, ΔH₂⁹⁸(ROOH−H) from experiment (Table 4), and ΔH₂⁹⁸[H] = 52.1028 ± 0.0014 kcal mol⁻¹. Their values were obtained from the experimental observation of the reaction of methyl radical with dioxygen [CH₃ + O₂ ↔ CH₃OO], for which the enthalpy was determined to be ΔH₂⁹⁸[H] = −23.7 ± 0.9 kcal mol⁻¹ by measurement of the forward and reverse rate constants. The agreement is excellent, especially for the ethyl and tert-butyl peroxy radicals for which Knayzev and Slag,12 who obtained ΔH₂⁹⁸[(CH₃)₂CO] = 2.2 ± 1.2 kcal mol⁻¹, their value was obtained from the experimental bond enthalpies (Table 4) and ΔH₂⁹⁸[H] = 52.1028 ± 0.0014 kcal mol⁻¹ for eq 30 gives heats of formation for the methyl, ethyl, and tert-butyl peroxyl radicals of ΔH₂⁹⁸[(CH₃)₂CO] = 4.8 ± 1.2 kcal mol⁻¹, ΔH₂⁹⁸[(CH₃)₂CH₂OO] = −6.8 ± 2.3 kcal mol⁻¹, and ΔH₂⁹⁸[(CH₃)₂CO] = −25.2 ± 2.5 kcal mol⁻¹. Therefore, our estimated lower limit for the heat of formation of the methyl peroxyl radical is 3.6 kcal mol⁻¹, which falls just outside the stated uncertainty of Knayzev and Slag,12 who obtained ΔH₂⁹⁸[(CH₃)₂CO] = 2.2 ± 1.2 kcal mol⁻¹. The uncertainty was obtained from the experimental bond enthalpies (Table 4) and ΔH₂⁹⁸[H] = 52.1028 ± 0.0014 kcal mol⁻¹, respectively. It is interesting to note that if we combine the ΔH₂⁹⁸[ROOH] values [where R = CH₃, CH₂CH₃, and (CH₃)₃C] derived from group additivity (Table 5) with our experimentally determined bond enthalpies, the resulting heats of formation, ΔH₂⁹⁸[(CH₃)₂CO] = 4.3 ± 1.4 kcal mol⁻¹, ΔH₂⁹⁸[(CH₃)₂CH₂OO] = −6.7 ± 2.4 kcal mol⁻¹, and

with recent high-level computational studies,\footnote{8,9} which suggest on the exothermicity of several important gas-phase reactions.

## Table 6. Experimental Electron Affinities, Acidities, Bond Energies and Term Energies for the Alkyl Peroxy Radicals, ROO, and Hydroperoxides, ROOH (All Values in kcal mol$^{-1}$)

<table>
<thead>
<tr>
<th>R</th>
<th>$EA[ROO]$</th>
<th>$\Delta_{acid}[H_2O][ROOH]$</th>
<th>$DH_{298}[ROOH]$</th>
<th>$DH_0[ROOH]$</th>
<th>$T_0[ROO]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>24.8 ± 0.1</td>
<td>376.7 ± 0.8</td>
<td>87.9 ± 0.8</td>
<td>86.7 ± 0.8</td>
<td>20.1 ± 0.2</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>26.8 ± 0.1</td>
<td>374.6 ± 1.0</td>
<td>87.8 ± 1.0</td>
<td>86.9 ± 1.0</td>
<td>21.1 ± 0.1</td>
</tr>
<tr>
<td>CH$_2$CH$_2$</td>
<td>27.3 ± 0.1</td>
<td>371.0 ± 2.2</td>
<td>84.8 ± 2.2</td>
<td>83.9 ± 2.2</td>
<td>21.6 ± 0.1</td>
</tr>
<tr>
<td>(CH$_3$)$_3$C</td>
<td>27.6 ± 0.3</td>
<td>370.2 ± 2.1</td>
<td>92.2 ± 2.1</td>
<td>83.3 ± 2.1</td>
<td>22.3 ± 0.3</td>
</tr>
</tbody>
</table>

$\Delta H_{298}[\text{CH}_3\text{C}_2\text{O}_2] = -25.8 ± 2.4$ kcal mol$^{-1}$, agree within the stated uncertainty with our "electron affinity/acidity/CBS" results.

Using the electron affinity/acidity/CBS-derived values for $\Delta H_{298}[\text{CH}_3\text{OO}], \Delta H_{298}[\text{CH}_3\text{CH}_2\text{OO}], \text{and } \Delta H_{298}[\text{CH}_3\text{C}_2\text{O}_2]$, it is possible to calculate the enthalpies of the reactions of dioxygen with methyl, ethyl, and tert-butyl radicals, respectively. The following heats of formation are employed for the alkyl radicals: $\Delta H_{298}[\text{CH}_3] = 34.9 ± 0.3$ kcal mol$^{-1}$, $\Delta H_{298}[\text{CH}_2\text{CH}_2] = 28.9 ± 0.4$ kcal mol$^{-1}$, and $\Delta H_{298}[\text{CH}_3\text{C}] = 12.4 ± 0.4$ kcal mol$^{-1}$.\footnote{60} With these auxiliary thermochemical values, we calculate $\Delta_{react}[H_2O][\text{CH}_3 + \text{O}_2 \rightarrow \text{CH}_3\text{OO}] = -30.1 ± 1.2$ kcal mol$^{-1}$, $\Delta_{react}[H_2O][\text{CH}_2\text{CH}_2 + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OO}] = -35.7 ± 2.3$ kcal mol$^{-1}$, and $\Delta_{react}[H_2O][\text{CH}_3\text{C} + \text{O}_2 \rightarrow \text{CH}_3\text{C}_2\text{O}_2] = -37.5 ± 2.5$ kcal mol$^{-1}$.\footnote{77} Our result for the reaction enthalpy of $[\text{CH}_3 + \text{O}_2]$ falls just outside the uncertainties reported by Knyazev and Slagle\footnote{12} (vide supra); however, the values for $[\text{CH}_2\text{CH}_2 + \text{O}_2]$ and $[\text{CH}_3\text{C} + \text{O}_2]$ fall within the uncertainties of $\Delta_{react}[H_2O][\text{CH}_2\text{CH}_2 + \text{O}_2] = -35.5 ± 2.0$ kcal mol$^{-1}$ and $\Delta_{react}[H_2O][\text{CH}_3\text{C} + \text{O}_2] = -36.5 ± 1.8$ kcal mol$^{-1}$ reported by these authors. This is significant agreement on the exothermicity of several important gas-phase reactions (reaction 8).

These experimental reaction enthalpies are in disagreement with recent high-level computational studies,\footnote{5,9} which suggest that the reaction is less exothermic with heats of reaction of just $-31.5$ or $-30.1$ kcal mol$^{-1}$ for $\Delta_{react}[H_2O][\text{CH}_3\text{CH}_2 + \text{O}_2]$. It should be reiterated that our value for the reaction enthalpy is not completely "experimental", since it depends in part on the computationally determined heat of formation of ethyl hydroperoxide. Comparing this value with other literature numbers (cf. Table 5) suggests that this is an upper limit and using any of the other cited values for deducing the heat of formation of the ethyl peroxy radical would generate a smaller value and consequently make reaction 8 more exothermic.

Table 6 summarizes the physical properties of the peroxy radicals (ROO) and their parent hydroperoxides (ROOH) as the alkyl group increases in size. These data reveal a number of trends that allow us to make some useful predictions about the physical properties of other, larger alkyl hydroperoxides and alkyl peroxy radicals. The electron affinities of the peroxy radicals (ROO) increase slightly as the substituent increases in size. This trend is subtle, however, with all electron affinities falling within 0.1 eV. Thus, we anticipate that alkyl peroxy radicals, whether linear or branched structures, will have $EA(\text{C}_n\text{H}_{2n+1}\text{OO}) = 1.2 ± 0.1$ eV. There is also a trend toward decreasing values of $\Delta_{react}[H_2O]$ with increasing length of the alkyl chain. Table 6 indicates that HOOH is the weakest acid of this series, followed by CH$_3$OOH, CH$_3$CH$_2$OOH, and (CH$_3$)$_3$COOH, which is the strongest acid. This trend is analogous to the behavior of the acidity of water and related, simple alkyl alcohols.\footnote{78} Excluding HOOH, the alkyl hydroperoxides demonstrate a decreasing bond enthalpy ($DH_{298}[ROO - \text{H}]$) with increasing R group size. This is clear when comparing $DH_{298}[\text{CH}_3\text{OO} - \text{H}]$ and $DH_{298}[\text{CH}_2\text{CH}_2\text{OO} - \text{H}]$, but the difference between $DH_{298}[\text{CH}_3\text{CH}_2\text{OO} - \text{H}]$ and $DH_{298}[\text{CH}_2\text{C}_2\text{O}_2 - \text{H}]$ is small compared with the stated uncertainties. However, although the absolute uncertainties for $DH_{298}[\text{CH}_2\text{CH}_2\text{OO} - \text{H}]$ and $DH_{298}[-\text{C}(\text{CH}_3)_2\text{C} - \text{O}_2] - \text{H}$ are large, it must be remembered that the relative uncertainties are much smaller ($\approx 0.4$ kcal mol$^{-1}$, see preceding discussion on gas-phase acidity), and thus the slight decrease in bond enthalpy is meaningful. This trend suggests that other alkyl hydroperoxides will have bond enthalpies similar to that of ethyl hydroperoxide ($DH_{298}[\text{C}_2\text{H}_5\text{OO}]$) as $85 ± 2$ kcal mol$^{-1}$.\footnote{41} Earlier authors\footnote{13} have suggested $88.6 ± 0.5$ kcal mol$^{-1}$ as a "universal" $DH_{298}[\text{ROO} - \text{H}]$ bond enthalpy; Table 6 indicates that $85 ± 2$ kcal mol$^{-1}$ is a more useful, conservative estimate.

### Acknowledgment.
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### Supporting Information Available:
Two tables giving molecular geometries, rotational constants, and harmonic frequencies calculated at the B3LYP/aug-cc-pVdz level of theory for ROO$^+$, ROO ($\tilde{x}$ and $\tilde{A}$), and ROOH (where $R = \text{CH}_3$, $\text{CD}_3$, and $\text{C}_2\text{H}_5\text{CH}_2$) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.