Quantum Chemical and Master Equation Simulations of the Oxidation and Isomerization of Vinoxy Radicals

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The vinoxy radical, a common intermediate in gas-phase alkene ozonolysis, reacts with O2 to form a chemically activated α-oxoperoxy species. We report CBS-QB3 energetics for O2 addition to the parent (CH2CHO, 1a), 1-methylvinooxy (CH3COCH2, 1b), and 2-methylvinooxy (CH2=CHCHO, 1c) radicals. CBS-QB3 predictions for peroxy radical formation agree with experimental data, while the G2 method systematically overestimates peroxy radical stability. RRKM/master equation simulations based on CBS-QB3 data are used to estimate the competition between prompt isomerization and thermalization for the peroxy radicals derived from 1a, 1b, and 1c. The lowest energy isomerization pathway for radicals 4a and 4c (derived from 1a and 1c, respectively) is a 1,4-shift of the acyl hydrogen requiring 19–20 kcal/mol. The resulting hydroperoxoacetyl radical decomposes quantitatively to form ·OH. The lowest energy isomerization pathway for radical 4b (derived from 1b) is a 1,5-shift of a methyl hydrogen requiring 26 kcal/mol. About 25% of 4a, but only ~5% of 4c, isomerizes promptly at 1 atm pressure. Isomerization of 4b is negligible at all pressures studied.

I. Introduction

The parent and substituted vinoxy (or oxoalkyl) radicals are key intermediates in both combustion1−3 and atmospheric4−7 chemistry. An important source of these species in the troposphere is the reaction of alkenes with ozone (or ozonolysis). Specifically, syn carbonyl oxides produced in ozonolysis are key intermediates in both combustion1−3 and atmospheric4−7 chemistry.

The kinetics of the reaction of unsubstituted vinoxy radical (1a) with O2, including the pressure dependence of the second-order rate coefficient, has been studied by Gutman and Nelson,24 by Lorenz et al.,25 and by Zhu and Johnston.26 Their data reveal a typical recombination mechanism, with falloff of the second-order rate coefficient being strongest between 10 and 100 Torr. All three groups determined low- and high-pressure-limit rate constants by fitting their data to Troe and co-workers’ classic expression.28

Miyoshi and co-workers27 have reported pressure-dependent kinetics measurements for the 1-methylvinooxy (1b) and 2-methylvinooxy (1c) systems. They have also applied Gaussian-2 (G2)29 and RRKM30 calculations to the pressure-dependent data25−27 to determine energy barriers (Eo,rec; see Scheme 2 below) and rate constants for the reactions of O2 with 1a, 1b, and 1c. Miyoshi and co-workers’ Eo,rec values are significantly lower than the barrier heights predicted31 by the CBS-QB332 and CBS-APNO33 composite electronic structure methods, with the energies for TS3b and TS3c below those of the separated methylvinooxy and O2 reactants. In this paper, we provide detailed quantum chemical evidence that these negative activation energies are artifacts of the G2 method’s overestimate of peroxy radical stability.

LIF studies of Gutman and Nelson24 and Lorenz et al.25 have provided experimental evidence that the 2-oxoethylperoxy radical (4a) decomposes to generate ·OH. Recent theoretical studies by Lee and Bozzelli3,31 and our laboratories33 attribute ·OH formation by 4a to the intramolecular abstraction of the acyl hydrogen:

Our master equation calculations31 on reaction 3 predicted that for the chemically activated 4a, ·OH formation is quantitative.
at low pressures (less than 10 Torr) and still significant at 1 atm pressure. Alkenes (such as cis- and trans-butene) whose ozonolysis produces acetaldehyde oxide can therefore generate up to two equivalents of *OH via reactions 1 and 3.

In this paper, we quantify the effect of alkyl substitution on the reactivity of the chemically activated α-oxoperoxy radical:

\[
\begin{align*}
R_2^-\text{O} + O_2 &\rightarrow R_2\text{O}^+ + \text{O}_2 \quad \text{(4)} \\
R_2^-\text{O} + O_2 &\rightarrow R_2\text{O}^+ + \text{O}_2 \quad \text{(5)}
\end{align*}
\]

Based on CBS-QB3 quantum chemical calculations and RRKM/master equation simulations, we determine to what extent prompt isomerization and decomposition to form *OH radical (reaction 4) compete with thermalization (reaction 5) for the 2-oxo-1-propylperoxy (4b; \(R_1 = CH_3, R_2 = H\)) and the 1-oxo-2-propylperoxy (4c; \(R_1 = H, R_2 = CH_3\)) radicals. This analysis allows us to assess the proficiency of vinoxy radicals as a tropospheric *OH source.

Our calculations also engage Kroll et al.’s report of *OD formation from the ozonolysis of 3-hexene deuterated at their vinylic positions:

\[
\begin{align*}
\text{D} &\rightarrow \text{CH}_2\text{C}D\text{O} \quad \text{(6)} \\
\text{D} &\rightarrow \text{CH}_2\text{C}D\text{O} \quad \text{(7)}
\end{align*}
\]

Kroll et al. argue that *OD radicals are formed in the isomerization and decomposition of anti carbonyl oxides (reaction 7). Based on model calculations on the deuterated parent vinylox radical 1a–d1, we proposed that the deuterated 2-methylvinoxy radical 1c–d1 formed in reaction 6 is another possible source of *OD:

\[
\begin{align*}
\text{C} &\rightarrow \text{CH}_2\text{C}D\text{O} \quad \text{(8)}
\end{align*}
\]

In this paper, we test this proposal by calculations on the actual intermediate formed in Kroll et al.’s experiments.

II. Theoretical Methods

A. Quantum Chemistry Calculations. All electronic structure calculations were performed with the Gaussian 98 suite of programs. The geometry and energy of each stationary point considered here were determined initially using the B3LYP functional and the 6-31G(d,p) basis set. The nature of each stationary point was then confirmed by calculating harmonic vibrational frequencies. Each minimum we report has all real frequencies, and each transition structure has one imaginary frequency. Animation of the imaginary frequency, sometimes combined with intrinsic reaction coordinate (IRC) calculations, enabled us to associate a given transition structure unequivocally with its reactant and product.

While a popular method for treating atmospheric oxidation reactions, the B3LYP method tends to underestimate hydrogen-shift reaction barriers and provide unreliable thermochemical predictions. Therefore, all of the species considered here were also treated with the CBS-QB3 model chemistry of Petersson and co-workers. This composite method employs optimized geometries and vibrational frequencies obtained at the B3LYP/6-311G(2d,d,p) level, treats electron correlation up to the CCSD(T)/6-31G(d′) level, and extrapolates the MP2 energy to the complete basis set limit. Recent studies indicate that CBS-QB3 often, but not invariably, provides excellent agreement with experimental reaction energies and barriers. The CBS-QB3 relative energies reported here are corrected for differences in zero-point vibrational energy scaled by 0.99.

To study the thermochemistry of peroxy radical formation, we also used Truhlar’s MPW1K hybrid density functional, Petersson’s CBS-APNO method, Pople’s Gaussian-2 (G2) and Gaussian-3 (G3) methods, and version 2m of Truhlar’s Multi-Coefficient G2 (MCG2) method. The vibrational contribution to 298 K enthalpies was scaled by 0.9989 for B3LYP/6-31G(d,p), 0.99 for the B3LYP/6-311G(2d,d,p) frequencies used by CBS-QB3, 0.9515 for MPW1K/6-31+G(d,p), and 0.8929 for the HF/6-31G(d) frequencies used by G2 and G3. The MCG2 method does not stipulate any particular method for the calculation of optimized geometries or frequencies. We chose to employ MP2(full)/6-31G(d) geometries (to facilitate comparison with the G2 predictions) and B3LYP/6-311G(2d,d,p) frequencies scaled by 0.99.

B. Statistical Rate Theory Calculations. We used Barker’s MultiWell program suite to solve the one-dimensional (internal energy) master equation for part of the vinoxy oxidation mechanism. The zero-point-corrected relative energies of all participating species were taken from our CBS-QB3 calculations. Unimolecular rate constants \(k(E)\) were computed using Rice–Ramsperger–Kassel–Marcus (RRKM) theory, with the required sums and densities of states being calculated with B3LYP/6-311G(2d,d,p) geometries and unscattered harmonic frequencies. We did not treat low-frequency internal rotations as hindered rotors, and our simulations included only the most stable conformer of each species. These simplifications will affect the numerical accuracy of our results but should not detract from the validity of our qualitative conclusions.

Collisional stabilization was treated using the exponential-down model with an average energy transferred per collision \((\langle E_d \rangle)\) assumed to be 300 cm\(^{-1}\). The bath gas was taken to be \(N_2\) at 298 K, with Lenard-Jones parameters of \(\sigma = 3.74\) Å and \(\epsilon = 82\) K. Each organic species was assigned ethylene oxide’s Lenard-Jones parameters of \(\sigma = 4.08\) Å and \(\epsilon = 421\) K. Each simulation was run for 1000 collisions to ensure that the pseudo steady state was achieved. However, only \(\sim 100\) collisions (corresponding to \(\sim 50\) ns at 1 atm pressure) was usually required for the concentrations of all participating species to remain constant to within the numerical noise of the simulation. More details of our rate calculations are given in section III.D below.

III. Results and Discussion

A. Structural Aspects of Vinoxy Oxidation. Figures 1–3 show our B3LYP/6-311G(2d,d,p) predictions for the geometries of all possible conformers of the species in reaction 2. (All
Structures have been rendered using the Ball & Stick program of Müller and Falk. When there is more than one conformer for a particular structural isomer, CBS-QB3 relative energies are also shown.

Figure 1 shows the B3LYP/6-311G(2d,d,p) structures of vinoxy (1a), 1-methylvinoxy (1b), and 2-methylvinoxy (1c) radicals. The existence of syn and anti conformers of 1c has been observed spectroscopically by Weisshaar and co-workers. Our calculations predict that although methyl substitution has no effect on the predicted C–O bond length, methyl substitution does increase the distance between the two sp²-hybridized carbons. In 1b, this C–C bond is 0.015 Å longer, and in the more stable conformer of 1c, this bond is 0.006 Å longer. The B3LYP/6-311G(2d,d,p) bond lengths for 1b and 1c agree to within 0.01 Å of the CASSCF/6-31G(d,p) predictions of Weisshaar and co-workers. The syn conformer of 1c is predicted to be 0.6 kcal/mol lower in energy than the anti conformer, in excellent agreement with CASSCF/6-31G(d,p) relative energies. This preference for the syn form is consistent with Wiberg and Martin’s prediction that the synperiplanar conformer of propanal is more stable than its anticlinal conformer. Wiberg and Martin attribute this preference to the C_dO (permanent) bond dipole’s inducing a dipole in the synperiplanar methyl group.

Figures 2 and 3 show the possible conformers of the addition transition structures. The anticlinal (I) and synclinal (II) conformers of TS3a (Figure 2) are nearly identical in energy. Structure TS3b (Figure 2) exists as a single conformer. For TS3c (Figure 3), the structure with the O₂ syneriplanar to the C₆–C₅ bond (I) is 2.3 kcal/mol more stable than the structure with the O₂ antiperiplanar to the C₆–C₅ bond (II). In I, the free O atom is rather close to the C–H bond pointing out of the plane of the 2-methylvinoxy radical (r(H–O) = 2.168 Å). This proximity permits the donation of electron density from the ð* HOMO of O₂ to the ð* orbital of the interacting C–H bond. This favorable interaction preferentially lowers I’s energy. Evidence for this interaction includes the following: (1) the O–O bond length is 0.005 Å shorter in I than in II; (2) the interacting C–H bond in I is ~0.01 Å longer than the other two C–H bonds on the 2-methyl substituent; (3) the C–H stretch frequency of the interacting bond in I is 140–210 cm⁻¹ to the red of the other two C–H stretches in I.
Figures 4–6 show the predicted geometries of the oxoalkyloxy radicals 4a, 4b, and 4c. The 2-oxoethylperoxy radical 4a has four possible conformers (Figure 4). Structures I and IV, whose $\delta_\alpha$–$\delta_\beta$ bonds are synclinal to the C–C bonds, possess C–C bonds $\approx 0.01$ Å longer than those of structures II and III, whose $\delta_\alpha$–$\delta_\beta$ and C–C bonds are antiperiplanar. This suggests that in I and IV, one of the lone pairs on the $\alpha$-oxygen, which is antiperiplanar to the C–C bond, delocalizes into the $\sigma^*(C=C)$ orbital (see Scheme 1). This anomic-like effect, combined with the electrostatic preference for antiparallel C–O bond dipoles, makes I the most stable structure. The most stable conformer of the 2-oxo-1-propylperoxy (or acetonylperoxy) radical 4b (Figure 5) also benefits both from synclinal O–O and C–C bonds and from antiparallel C–O bonds. All three conformers of the 1-oxo-2-propylperoxy radical 4c (Figure 6) have synclinal O–O and C–C bonds, with the two lowest-energy structures (I and II) also containing antiperiplanar C–O bond dipoles.

B. Energetics of Vinoxy Oxidation. Table 1 summarizes both our CBS-QB3 and Miyoshi and co-workers’ predictions for the energy diagram in Scheme 2. All relative energies are based on the most stable conformer of each species.

Miyoshi and co-workers used RRKM/master equation calculations, based on B3LYP/6-31G(d) molecular parameters, to fit the pressure dependence of the experimental second-order rate coefficients for the oxidation reaction. Their simulations also employed G2 calculations of the (experimentally unmeasured) reaction energies. This analysis allowed them to estimate the threshold energy required to dissociate the adduct to vinoxy radical and molecular oxygen.

The G2 reaction energies were added to the threshold energies to derive the forward barriers ($E_{rec}$) for the recombination of vinoxy radical and $O_2$. The negative barriers for 1b and 1c are rather surprising, given that transition structures (that is, first-order saddle points) for $O_2$ addition are predicted by Miyoshi and co-workers to exist on the B3LYP surface at energies above those of the separated reactants. More fundamentally, the loss
TABLE 2: Predictions of Zero-Point-Corrected Energies (kcal/mol) for Scheme 2

<table>
<thead>
<tr>
<th>system</th>
<th>R1</th>
<th>R2</th>
<th>RRKM threshold E°</th>
<th>G2 reaction E°</th>
<th>$E_{\text{rec}}$</th>
<th>CBS-QB3 barrier</th>
<th>CBS-QB3 reaction E</th>
<th>adjusted $E_{\text{rec}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>H</td>
<td>H</td>
<td>27.6</td>
<td>-26.8</td>
<td>+0.8</td>
<td>+4.3</td>
<td>-22.9</td>
<td>+4.7</td>
</tr>
<tr>
<td>b</td>
<td>CH₃</td>
<td>H</td>
<td>28.3</td>
<td>-28.9</td>
<td>-0.6</td>
<td>+2.4</td>
<td>-25.0</td>
<td>+3.3</td>
</tr>
<tr>
<td>c</td>
<td>H</td>
<td>CH₃</td>
<td>26.1</td>
<td>-26.9</td>
<td>-0.8</td>
<td>+4.1</td>
<td>-22.6</td>
<td>+3.5</td>
</tr>
</tbody>
</table>

* From ref 27. ** From ref 31. † From this work. ‡ The sum of the RRKM threshold energy and the CBS-QB3 reaction energy; see the text.

SCHEME 2

![Scheme 2](image)

TABLE 2: Theoretical and Experimental Enthalpy Changes (kcal/mol) for Reactions 9, 10, and 11

<table>
<thead>
<tr>
<th>method</th>
<th>reaction 9</th>
<th>reaction 10</th>
<th>reaction 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3LYP/6-31G(d,p)</td>
<td>-31.0°</td>
<td>-31.6°</td>
<td>-32.0°</td>
</tr>
<tr>
<td>MPW1K/6-31G+(d,p)</td>
<td>-29.6</td>
<td>-31.0</td>
<td>-31.8</td>
</tr>
<tr>
<td>CBS-APNO</td>
<td>-32.1</td>
<td>-34.7</td>
<td>-36.7</td>
</tr>
<tr>
<td>CBS-QB3</td>
<td>-33.0</td>
<td>-35.6</td>
<td>-37.6</td>
</tr>
<tr>
<td>G2</td>
<td>-33.5</td>
<td>-38.6</td>
<td>-41.1</td>
</tr>
<tr>
<td>MCG2</td>
<td>-32.3</td>
<td>-35.0</td>
<td>-37.1</td>
</tr>
<tr>
<td>G3</td>
<td>-32.2</td>
<td>-35.5</td>
<td>-38.1</td>
</tr>
<tr>
<td>CCSD(T)/TZ2P</td>
<td>-31.5°</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blanksby and Ellison°</td>
<td>-30.1 ± 1.2</td>
<td>-35.7 ± 2.3</td>
<td></td>
</tr>
<tr>
<td>Knyazev and Slagle°</td>
<td>-32.7 ± 0.9</td>
<td>-35.5 ± 2.0</td>
<td>-37.1 ± 2.3</td>
</tr>
</tbody>
</table>

* From ref 76; we predict a slightly different value for reaction 9. ** From ref 77. † From refs 73 and 74. ‡ From ref 75.

of vinoxy resonance stabilization (see below) required to form the peroxy radicals should lead to an enthalpic barrier. The prediction of negative barriers for the formation of 4b and 4c may be the artifact of a systematic error in the G2 calculations. An overestimate of the exothermicity of the peroxy formation reaction could lower the predicted energy of the transition structure below those of reactants. While there are no experimental thermochemical data on oxoalkylperoxy radicals, such data do exist for a variety of alkylperoxy radicals without oxo groups.73–75 Table 2 summarizes these data, as well as quantum chemical predictions of $\Delta H_{298}$ by us and two other groups,76,77 for reactions 9–11.

-CH₃ + O₂ → CH₃OO· [9]

-CH₂CH₃ + O₂ ↔ H₂O· [10]

-CH₂CH₂CH₃ + O₂ ↔ H₂O· [11]

As compared to Blanksby and Ellison’s value73,74 for ethylperoxy and Knyazev and Slagle’s value75 for all three systems, the B3LYP and MPW1K hybrid density functional methods underestimate the stability of alkylperoxy radicals relative to their O₂ and alkyl radical constituents.78 The single-level ab initio CCSD(T)/TZ2P calculation of Schaefer and co-workers77 also underestimates the stability of ethylperoxy radical, as judged by either experimental value. This is despite geometries optimized at the very high CCSD(T)/DZP level.

In contrast, the composite CBS-APNO and CBS-QB3 methods (both used extensively in our previous study75 of the parent vinoxy radical) predict exothermicities for reactions 9–11 that agree with experiment to within the experimental uncertainties (except for Blanksby and Ellison’s73,74 $\Delta H_{298}$ for eq 9). In contrast, the G2 method overestimates the stability of all three alkylperoxy radicals considered. However, if the very same components (except the higher level correction) that are summed to determine the G2 energy are instead summed using Truhlar’s MCG257,58 weighting coefficients, the resulting reaction energies all agree with experiment. Pople’s Gaussian-3 (G3) method56 also fixes this systematic error in G2.

It is reasonable to assume that G2 also overestimates the stability of oxo-substituted alkylperoxy radicals 4a, 4b, and 4c. This motivates a re-evaluation of the forward barrier for the oxidation of vinoxy radicals 1a, 1b, and 1c. If we combine Miyoshi and co-workers’ RRKM threshold energies27 and our CBS-QB3 reaction energies, we obtain “adjusted” $E_{\text{rec}}$ values (last column of Table 1) that agree to within 1 kcal/mol of the CBS-QB3 barriers.

Alternatively, it is important to note that Miyoshi and co-workers’ prediction of negative barriers for the formation of 4b and 4c was based on a scheme which did not include the isomerization of 4b and 4c (discussed in sections C and D below). It is possible that a model of the pressure dependence of the experimental25–27 second-order rate coefficients for the oxidation reaction that included peroxy radical isomerization would lead to positive reaction barriers even with the G2 method.

We also observe that the formation of oxoalkylperoxy radicals is several kcal/mol less exothermic than the formation of the alkylperoxy radicals considered in Table 2. The most important reason for this difference is that adding O₂ to vinoxy radicals causes them to lose resonance stabilization, while adding O₂ to localized alkyl radicals engenders no such loss. To quantify this effect, we propose the following definition of resonance stabilization energy: the difference between (1) the energy required to break the appropriate C–H bond in an aldehyde or ketone to form the delocalized vinoxy radical 1a, 1b, or 1c and (2) the energy required to break the analogous C–H bond in the analogous alcohol. Scheme 3 shows the specific reactions studied, and Table 3 contains the CBS-QB3 energetics.

Table 3 indicates that conjugation in the parent and methyl-substituted vinoxy radicals affords a 7–10 kcal/mol advantage over analogous localized α-hydroxyalkyl radicals. Bouchoux et al.29 and Espinosa-Garcia et al.30 have also reported resonance stabilization energies for 1a and 1b. However, both groups employ Baird et al.’s81 original definition in that they compare vinoxy radicals to unsubstituted alkyl radicals. With this approach, they obtain stabilization energies of only 4–6 kcal/mol.
The oxo group that stabilizes vinoxy radicals $1a$, $1b$, and $1c$ has the opposite effect on the peroxy radicals $4a$, $4b$, and $4c$. Brinck et al. predict that such electron-withdrawing groups slightly destabilize peroxy radicals. This effect also helps explain the smaller exothermicity of oxoalkylperoxy radical formation.

C. Intramolecular Hydrogen Shifts in α-Oxoalkylperoxy Radicals. We considered all possible intramolecular hydrogen abstraction reactions for the three oxoalkylperoxy radicals. The parent system $a$ can undergo a 1,4-H shift (via TS5a) or a 1,3-H shift (via TS6a):

System $b$ can undergo a 1,3-H shift (via TS6b) or a 1,5-H shift (via TS7b):

System $c$ can undergo a 1,4-H shift (via TS5c), a 1,3-H shift (via TS6c), or a 1,5-H shift (via TS7c):

Figures 7–9 show the geometries of the transition structures for reactions 15–21, and Table 4 contains the energies (relative to reactants $4a$, $4b$, or $4c$) of the most stable conformers of the transition structures and products for these reactions.

The most facile isomerization is the 1,4-shift (TS5a and TS5c) of the acyl hydrogen, with barriers of 19–20 kcal/mol. The more strained 1,3-hydrogen shift transition structures (TS6a, TS6b, and TS6c) are 18–20 kcal/mol higher in energy. The 1,5-hydrogen shift transition structures (TS7b and TS7c) are 7–16 kcal/mol higher in energy than TS5a and TS5c, even though TS7b and TS7c have less torsional strain. This reflects the fact that acyl C–H bonds are ~10 kcal/mol weaker than primary C–H bonds. Other correlations between reaction barrier and reaction energy can be seen in the set of 1,3-hydrogen shifts (compare energies of TS6 and 9) and the pair of 1,5-hydrogen shifts (compare energies of TS7 and 10).

D. Kinetics of Oxoalkylperoxy Radical Isomerization. We solved the master equation for the chemically activated peroxy radicals $4a$, $4b$, and $4c$. Our goal was to quantify the competition between the prompt intramolecular hydrogen shift and the collisional stabilization of $4a$, $4b$, and $4c$ as a function of bath gas pressure. Scheme 4 shows the energy diagram treated in the master equation calculations, and Table 5 summarizes the CBS-QB3 threshold energies used.

The entrance channel is the addition of O$_2$ to a given vinoxy radical, with the initial energy of each oxoalkylperoxy radical being represented by a shifted thermal distribution truncated at threshold energy $E_{o,rev}$. The exit channel is the lowest-barrier
isomerization available to that radical (reactions 15, 18, and 19 above). Reactions 15 and 19 form the hydroperoxyacyl radicals $8a$ and $8c$, respectively. Reaction 18 forms the hydroperoxyvinoxy radical $10b$. We assumed in each case that the hydrogen shift was irreversible. (This assumption will be discussed in section E.)

Table 5: CBS-QB3 Zero-Point-Corrected Threshold Energies (kcal/mol) for Scheme 4

<table>
<thead>
<tr>
<th>system</th>
<th>$E_{o,rev}$</th>
<th>$E_{o,for}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>+27.3</td>
<td>+19.5</td>
</tr>
<tr>
<td>b</td>
<td>+27.4</td>
<td>+26.1</td>
</tr>
<tr>
<td>c</td>
<td>+26.7</td>
<td>+18.6</td>
</tr>
</tbody>
</table>

Figures 10–12 show the pseudo steady-state relative yields of thermalized peroxo radical and hydrogen shift product for the three systems. One thousand simulations were run for each bath gas pressure, producing relative yields reproducible to two decimal places.

As we reported earlier, prompt formation of the hydroperoxyacetyl radical $8a$ falls off rather slowly with increasing pressure, with $\sim$25% of $4a$ predicted to isomerize even at 1 atm (Figure 10). Prompt formation of the 2-hydroperoxypropanoyl radical $8c$ falls off much more rapidly with increasing pressure, with $\leq10\%$ of $4c$ predicted to isomerize for pressures above 400 Torr (Figure 12). Although $4a$ and $4c$ have very similar reaction barriers (Table 5), $4c$'s additional methyl group slows its isomerization rate by a factor of $\sim3$. The 7–8 kcal/mol higher barrier for the methyl hydrogen abstraction in $4b$
TABLE 6: Hydrogen Shift Thermal (298 K) Unimolecular Rate Constants

<table>
<thead>
<tr>
<th>reactant</th>
<th>$A_\infty (s^{-1})$</th>
<th>$k (s^{-1})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>$1.61 \times 10^{12}$</td>
<td>$8.16 \times 10^{-3}$</td>
</tr>
<tr>
<td>4b</td>
<td>$4.39 \times 10^{10}$</td>
<td>$3.23 \times 10^{-8}$</td>
</tr>
<tr>
<td>4c</td>
<td>$1.60 \times 10^{12}$</td>
<td>$3.71 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

makes the prompt formation of 10b negligible under all pressures studied (Figure 11). Orlando et al. \(^{84}\) come to the same conclusion regarding 4b based on B3LYP/6-31G(d,p) and RRKM calculations.

We tested the sensitivity of our relative yield predictions to a factor of 3 variation in the average energy transferred per collision ($\langle E_d \rangle$) and a ±10% variation in the CBS-QB3 threshold energies (Table 5). These changes caused the 1-atm yield of 8a to vary from 5% to 70% and the 1-atm yield of 8c to vary from 0% to 50%. Yields of 10b remained zero within the uncertainty of our simulations. Variation of the Lennard-Jones parameters by ±20% caused no statistically significant variation in any yields.

We used our CBS-QB3 reaction barriers and B3LYP/6-311G-(2d,d,p)-derived partition functions to estimate the thermal rate constants for the lowest barrier hydrogen shifts. Table 6 shows that all three oxalkylperoxy radicals will isomerize slowly at 298 K; the shortest lifetime with respect to the hydrogen shift is ~30 s for 4c. In the atmosphere, all three peroxy radicals, once thermalized, will preferentially undergo bimolecular reactions.

Possible bimolecular reactions of 4a were discussed previously.\(^{31}\) The chemistry of 4b has been rather well-studied.\(^{85}\) Both the self-reaction of 4b and its reaction with NO form the chemically activated acetonoxo radical 11:

$$\begin{align*}
n\text{O} \cdot + \text{O}_3 &= \text{O} \cdot + \text{O} + \text{O}_2 \quad [22] \\
n\text{O} \cdot + \text{NO} &= \text{O} \cdot + \text{NO}_2 \quad [23]
\end{align*}$$

Calculations by Orlando et al.\(^ {84}\) predict that about 80% of 11 decomposes to acetyl radical and formaldehyde under tropospheric conditions. The chemistry of 4c has received little attention to date, but workers have proposed reactions similar to eqs 22 and 23.\(^ {86}\)

E. Structure and Reactivity of the Hydroperoxyacyl Radical. Figure 13 shows the possible conformers of the acyl radicals 8a and 8c formed by prompt isomerization of 4a and 4c, as discussed in the previous section. In conformer I of both 8a and 8c, the intramolecular hydrogen bond overcomes the electrostatic repulsion between synperiplanar C–O bond dipoles. Hydrogen bonding in 8a confers a net stabilization of 1.7 kcal/mol. In contrast, hydrogen bonding in 8c confers virtually no net stabilization. One possible reason is that conformer 8c-II, unlike conformer 8a-II, benefits from a small dipole–induced dipole interaction between the C–O bond and the syngel methyl group. (This analysis, due to Wiberg and Martin,\(^ {32}\) was discussed above for the 2-methylvinoxy radical.)

Table 7 summarizes the CBS-QB3 energetics for the lowest barrier decomposition pathways for acyl radicals 8a and 8c.

![Figure 13. Structures of the hydroperoxyacyl radicals 8a and 8c.](image)

<table>
<thead>
<tr>
<th>system</th>
<th>8</th>
<th>TS12</th>
<th>13+14</th>
<th>TS15+14</th>
<th>16+17+14</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.0</td>
<td>+11.4</td>
<td>+6.4</td>
<td>+5.7</td>
<td>−27.3</td>
</tr>
<tr>
<td>c</td>
<td>0.0</td>
<td>+9.7</td>
<td>+6.4</td>
<td>+6.0</td>
<td>−30.6</td>
</tr>
</tbody>
</table>

(reaction 24). Figure 14 shows predicted structures for the C–C $\beta$-scission transition states (TS12), the hydroperoxyalkyl radicals (13), and the O–O $\beta$-scission transition states (TS15).

The methyl substituent in system c lowers the energy of TS12 by ~2 kcal/mol and makes the overall decomposition of the acyl radical more exothermic by ~3 kcal/mol. The methyl substituent also lengthens the C$_3$–O$_1$ bond by ~0.01 Å throughout the reaction coordinate. As we\(^ {31}\) and others\(^ {37,87,88}\) have noted before, the ipso hydroperoxyalkyl radical (13) has an electronic energy only a fraction of a kcal/mol lower than its $\beta$-scission transition structure (TS15), and the zero-point correction, based on harmonic vibrational frequencies, drops the energy of TS15 below that of 13.
The acyl radicals $8a$ and $8c$ are significantly chemically activated, with internal energy of $\geq 20$ kcal/mol. Moreover, their decomposition transition states $TS12$ and $TS15$ are rather low in energy and rather high in entropy. It is therefore reasonable to assume that 100% of $8a$ and $8c$ will decompose promptly under atmospheric conditions to give an equivalent of $^1$OH. Hence, the formation of $8a$ and $8c$ is irreversible.

**F. Formation of $^1$OD Radicals.** Finally, we consider our proposal that the 1-oxo-2-propylperoxy radical deuterated at the acyl position (4c-$d_1$) could be a source of $^1$OD in Kroll et al.’s experiments via reaction 8:

$$\begin{align*}
\text{HO}_2 + O_2 & \rightarrow \text{HO}_2^\text{+} + O_2^- \\
^1\text{OD} & \rightarrow \text{CH}_2\text{CHO} + CO + ^1\text{OD} \\
1\text{c-d}_1 & \rightarrow 4\text{c-d}_1 & \rightarrow 8\text{c-d}_1 & \rightarrow \text{CH}_2\text{CHO} + CO + ^1\text{OD} & [8]
\end{align*}$$

We performed RRKM/master equation simulations on 4c-$d_1$ using the energetics for 4c (Table 5) and the B3LYP/6-311G-(2d,d,p) moments of inertia and vibrational frequencies for the participating deuterated species (Scheme 5). At 6 Torr (the pressure in Kroll et al.’s LIF experiments), the yield of 8c-$d_1$ is $\sim 100\%$. As discussed in Section E, we can expect all of the 8c-$d_1$ to decompose to afford $^1$OD. Therefore, the ozonolysis of 3-hexenes with vinylic deuteriums should produce $^1$OH and $^1$OD radicals in a 1 to 1 ratio. (This assumes that each equivalent of syn propanal oxide produces 1 equivalent of $^1$OH and 1 equivalent of 4c-$d_1$ and each equivalent of 4c-$d_1$ produces 1 equivalent of $^1$OD.) In contrast, Kroll et al. report $^1$OH/$^1$OD ratios of $2:1$ for cis-3-hexene and $7:1$ for trans-3-hexene.

Clearly, our theoretical model significantly overestimates the yield of 8c-$d_1$ (and therefore of $^1$OD). A number of factors may contribute to this error: (1) We treat only the lowest-energy conformers in Scheme 5. This simplification underestimates the entropy of intermediate 4c-$d_1$ more than the entropy of transition state TS5c-$d_1$ because the oxo group of 4c-$d_1$, unlike that in

**IV. Conclusions**

Our B3LYP/6-311G(2d,d,p) calculations indicate that the lowest energy conformers are stabilized by antiparallel bond dipoles, dipole-induced dipole interactions, and delocalization of electron density out of lone pair or antibonding orbitals. For hydroperoxy species such as $8a$ and $8c$ (Figure 13), intramolecular hydrogen bonding to the carbonyl oxygen more than compensates for the electrostatic repulsion between parallel bond dipoles.

The loss of resonance stabilization in both the parent and methyl-substituted vinoxy radicals impedes their reactivity with O$_2$ (reaction 2 above). CBS-QB3 calculations predict reaction barriers of 2–4 kcal/mol and reaction energies of $\sim 23$ to $\sim 25$ kcal/mol (Table 1). In contrast, the addition of O$_2$ to unconjugated alkyl radicals is barrierless, and reaction energies are several kcal/mol more exothermic (Table 2). Experimental thermochemical data$^{73–75}$ for alkylperoxy radicals help validate CBS-QB3 predictions for the energetics of reaction 2. In general, both complete basis set and Gaussian-$n$ quantum chemical methods are more reliable for peroxy radicals than single-level ab initio methods, even if the latter employ very high-level ab initio geometries.

The ultimate validation of the CBS-QB3 predictions requires a detailed modeling of the experimental falloff curves for the vinoxy oxidation reactions. Accurate calculation of the vinoxy + O$_2$ rate constants would require rigorous methods such as variational transition state theory$^{93}$ and is beyond the scope of the current investigation.

Experiment$^{24,25}$ and theory$^{1,31}$ indicate that under atmospheric conditions, the parent vinoxy radical $1a$ will be a significant nonphotochemical source of $^1$OH (Figure 10). The 2-methylvinnoxy radical $1c$ will be a significant $^1$OH source only at low pressures (Figure 12). Larger substituents at the 2-position or alkyl substituents at the 1-position (as in the 1-methylvinnoxy radical $1b$) render $^1$OH production from vinoxy radical negligible (Figure 11). Therefore, in alkene ozonolysis, the formation of two equivalents of $^1$OH per equivalent of alkene is an issue only when syn acetaldehyde oxide or syn propanal oxide, the precursors of $1a$ and $1c$, is produced.
The production of hydroxyl radical from the oxidation of $\text{I}_\text{c}$ provides a qualitative explanation for the observation of $\cdot\text{OD}$ in the ozonolysis of 3-hexenes with vinyl deuterium.$^{34}$ A quantitatively accurate master equation simulation would require more rigorous quantum chemistry methods and treatment of all possible conformers. The former is especially important given the high sensitivity of relative yield predictions to small changes in reaction barriers. Moreover, the large difference in the $\cdot\text{OD}$ ratios for cis- and trans-3-hexene suggests that other factors, such as the difference in the chemical activation of carbonyl oxides formed from cis- vs trans-3-hexene and the production of $\cdot\text{OD}$ from anti carbonyl oxides, must also be considered. Computational studies of the above issues are ongoing.

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References and Notes


Moreover, Knyazev and Slagle’s data demonstrate a 2.8 kcal/mol increase in the stability of ethylperoxy vs methylperoxy, and another 1.6 kcal/mol increase in the stability of isopropylperoxy vs ethylperoxy. The hybrid DFT methods predict at most half of the observed substituent effect. Truhlar and co-workers (Dybala-Defratyka, A.; Paneth, P.; Pu, J.; Truhlar, D. G. J. Phys. Chem. A 2004, 108, 2475) have recently observed the same problem in B3LYP and MPW1K’s treatment of hydrogen transfers between alkyl radicals.

