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# Computational Studies of the Isomerization and Hydration Reactions of Acetaldehyde Oxide and Methyl Vinyl Carbonyl Oxide

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Alkene ozonolysis is a major source of hydroxyl radical ( $\bullet\text{OH}$ ), the most important oxidant in the troposphere. Previous experimental and computational work suggests that for many alkenes the measured  $\bullet\text{OH}$  yields should be attributed to the combined impact of both chemically activated and thermalized *syn*-alkyl Criegee intermediates (CIs), even though the thermalized CI should be susceptible to trapping by molecules such as water. We have used RRKM/master equation and variational transition state theory calculations to quantify the competition between unimolecular isomerization and bimolecular hydration reactions for the *syn* and *anti* acetaldehyde oxide formed in *trans*-2-butene ozonolysis and for the CIs formed in isoprene ozonolysis possessing *syn*-methyl groups. Statistical rate theory calculations were based on quantum chemical data provided by the B3LYP, QCISD, and multicoefficient G3 methods, and thermal rate constants were corrected for tunneling effects using the Eckart method. At tropospheric temperatures and pressures, all thermalized CIs with *syn*-methyl groups are predicted to undergo 1,4-hydrogen shifts from 2 to 8 orders of magnitude faster than they react with water monomer at its saturation number density. For thermalized *anti* acetaldehyde oxide, the rates of dioxirane formation and hydration should be comparable.

## I. Introduction

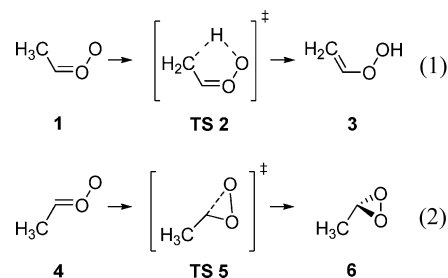
The reaction of ozone with alkenes, known as ozonolysis, is a significant nonphotochemical source<sup>1–6</sup> of hydroxyl radical ( $\bullet\text{OH}$ ), the most important oxidant in the troposphere.<sup>7,8</sup> A comprehensive understanding of tropospheric chemistry thus depends on a complete and accurate characterization of the ozonolysis mechanism. Quantum chemical and statistical rate theory methods, if validated, can be powerful tools for constructing such mechanisms. Scheme 1 presents the initial steps of ozonolysis for one of the alkenes considered in this paper, *trans*-2-butene. We chose to model *trans*-2-butene because of the availability of experimental data to validate our predictions.

The large exothermicity ( $\Delta_r H^\circ \approx -55$  kcal/mol) of primary ozonide formation leads to chemical activation of the resulting carbonyl oxide (or Criegee Intermediate, CI). For small alkenes such as *trans*-2-butene, a significant fraction of the nascent CI distribution possesses energy in excess of the barriers to unimolecular reaction, enabling the CI to isomerize promptly, that is, on the sub-microsecond time scale.<sup>9,10</sup>

The particular unimolecular pathway taken by the CI is largely controlled by its conformation (Scheme 2). A chemically activated CI with an alkyl group *syn* to the peroxy bond preferentially isomerizes via a 1,4-hydrogen shift to a vinyl hydroperoxide. The hydroperoxide is likewise chemically activated and should therefore decompose promptly to form a vinyloxy radical and  $\bullet\text{OH}$ .<sup>11–13</sup> The *syn*-alkyl CI thus functions as an  $\bullet\text{OH}$  precursor in the ozonolysis mechanism. In contrast, a chemically activated CI lacking a *syn*-alkyl group will typically isomerize to a dioxirane.<sup>14–16</sup> This dioxirane will preferentially isomerize to a carboxylic acid.<sup>16</sup> Although the acid is highly activated, it is likely<sup>16–21</sup> that this species does not undergo homolysis to form  $\bullet\text{OH}$ . However, Kroll et al.<sup>22</sup> have reported experimental evidence that in the ozonolysis of some alkenes

the acid derived from *anti* CI may release  $\bullet\text{OH}$ . Nguyen et al.<sup>23,24</sup> have also reported computational evidence that dioxiranes may access a low-barrier intersystem crossing to a triplet *bis*(oxy) diradical that, in the case of the dioxirane derived from acetaldehyde oxide, would lead ultimately to  $\text{CO}_2$ ,  $\bullet\text{CH}_3$ , and  $\bullet\text{H}$ . While consideration of this pathway for the CIs considered here is beyond the scope of this paper, it certainly merits future study.

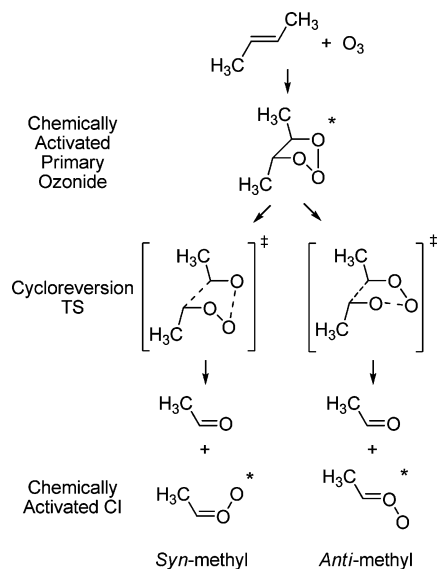
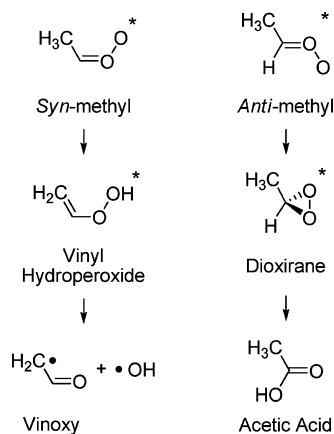
In the atmosphere, and in smog chamber experiments, the fraction of CI that does not isomerize promptly will be thermalized by collisions with background gas. The conformational preferences shown in Scheme 2 apply even more rigidly to thermalized CI, as shown in reactions 1 and 2:



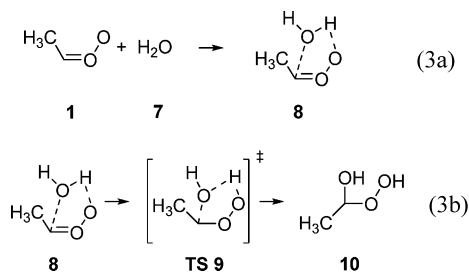
Although the initial distribution of vinyl hydroperoxide **3** formed in the thermal reaction of **1** will not be as activated as that formed from chemically activated **1**, all of **3** is nevertheless expected to decompose quantitatively to  $\bullet\text{OH}$  and a vinyloxy radical.<sup>9</sup> However, Johnson and Marston<sup>25</sup> have recently discussed the possibility that some fraction of the vinyl hydroperoxide formed in the ozonolysis of 2,3-dimethyl-2-butene may be collisionally stabilized under atmospheric conditions. We return to this possibility later.

In contrast to chemically activated CI, the isomerization of thermalized CI takes place on the millisecond time scale or

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SCHEME 1: *Trans*-2-Butene OzonolysisSCHEME 2: *Syn* and *Anti* Acetaldehyde Oxide

longer. This means that bimolecular reactions of CI may be comparable in rate.<sup>26</sup> In the atmosphere, the most important bimolecular reaction will be with water. Hydration of *syn* acetaldehyde oxide proceeds as shown in reactions 3a and 3b:



Quantum chemistry calculations by Anglada et al.,<sup>27</sup> Paulson and co-workers,<sup>28</sup> and Ryzhkov and Ariya<sup>29</sup> indicate that hydration begins with the formation of hydrogen-bonded complex **8**, followed by formation of  $\alpha$ -hydroxy hydroperoxide **10**. Paulson and co-workers<sup>28</sup> also provided experimental and computational evidence that the saturated hydroperoxide **10** will not be a labile source of •OH, unlike the unsaturated hydroperoxide **3** formed in reaction 1. Hence, if the *syn*-alkyl CI **1** is trapped by water (via reactions 3a and

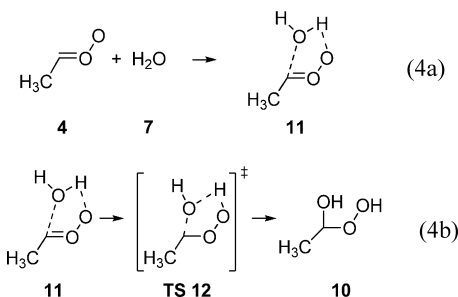
3b) before it can isomerize (via reaction 1), species **1** will not produce •OH.

Moreover, experiments indicate that the •OH yield from alkene ozonolysis is independent of relative humidity (RH) for ethene,<sup>28</sup> *trans*-2-butene,<sup>28</sup> 2-methyl-2-butene,<sup>30</sup> and several terpenes.<sup>31</sup> These studies suggest that many thermalized *syn*-alkyl CIs undergo the 1,4-hydrogen shift faster than they can react with water. Kroll et al.<sup>10</sup> performed time-dependent RRKM/master equation calculations on a series of CIs, providing strong evidence that the isomerization and decomposition of both vibrationally excited and thermalized *syn*-alkyl CIs should contribute to •OH formation in the troposphere. Recent computational work by Nguyen et al.<sup>24</sup> on  $\beta$ -pinene ozonolysis also supports the contention that thermalized *syn*-alkyl CIs form •OH. However, there are no studies in the literature directly comparing the kinetics of the unimolecular and bimolecular reactions of CIs.

In this paper, we use highly accurate quantum chemical calculations, variational transition state theory (TST), and the Eckart tunneling model to predict high-pressure limit thermal rate constants for the 1,4-hydrogen shift and hydration reactions for *syn* acetaldehyde oxide (**1**). We predict that in the temperature range found in the troposphere, the 1,4-hydrogen shift, and therefore •OH formation, proceeds 3–8 orders of magnitude (at the high-pressure limit) faster than the reaction of **1** with water monomer at its saturation vapor pressure. Estimates of the falloff curves for the 1,4-hydrogen shift indicate that this reaction is close to its high-pressure limit at the pressures found in the troposphere. In this study, we did not perform calculations on the reaction of **1** with water dimer. However, we will consider the important results of Ryzhkov and Ariya<sup>29</sup> on water dimer reactions.

Recent experimental work by Wegener et al.<sup>32</sup> suggests that RH can have a significant effect on the •OH yields from the ozonolysis of propene, 1-butene, 2-methylpropene, and *cis*-2-butene. Although Wegener et al.'s results do not contradict the predictions reported here, we will still discuss the broader implications of their results at the end of this paper.

We also consider the hydration of *anti* acetaldehyde oxide (**4**):

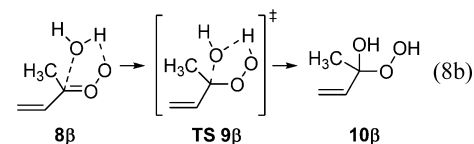
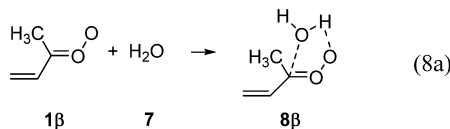
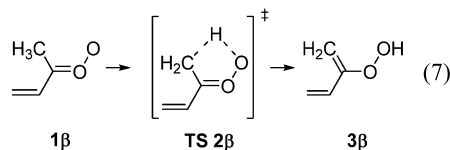
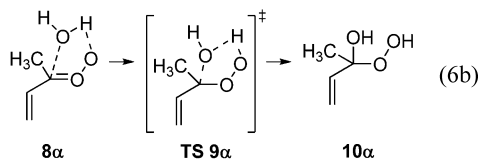
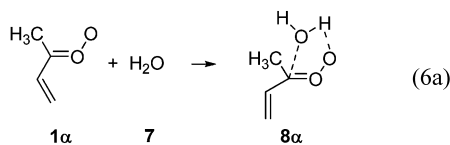
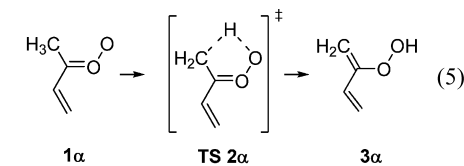


We predict that at 298 K the *anti* conformer reacts ~40 000 times faster with water than does the *syn* conformer. This is consistent with the transition state theory predictions of Anglada et al.<sup>27</sup> and of Ryzhkov and Ariya.<sup>29</sup> We also predict that at 298 K and at 100% RH the hydration of *anti* acetaldehyde oxide proceeds around three times faster than closure to the dioxirane (reaction 2 above). This is consistent with the recent analysis of Johnson and Marston.<sup>25</sup>

In addition to our TST predictions, we also report RRKM/master equation simulations of the formation and isomerization of both conformers of acetaldehyde oxide. These calculations enable us to explain three key experimental results for *trans*-2

-butene ozonolysis: (1) With one exception,<sup>33</sup> experimentalists<sup>5,28,32,34–37</sup> have constrained the •OH yield to lie between 0.52 and 0.70. (2) Paulson and co-workers<sup>26</sup> have estimated a combined isomerization rate constant for *syn* and *anti* acetaldehyde oxide derived from *trans*-2-butene to be 76 s<sup>−1</sup>, with a confidence interval of [25 s<sup>−1</sup>, 230 s<sup>−1</sup>]. (Note that this experimental study did not directly probe either the CI or its putative isomerization products.) (3) Paulson and co-workers<sup>38</sup> have estimated a stabilized Criegee intermediate (SCI) yield of 0.24 ± 0.07 using H<sub>2</sub>O as a scavenger. Our predictions are all broadly consistent with these experimental results.

Finally, we report some predictions for the ozonolysis of isoprene, the most abundant alkene in the troposphere.<sup>39</sup> We use TST to compute thermal rate constants for the isomerization and hydration of the two conformers of methyl vinyl carbonyl oxide, **1α** and **1β**, responsible for •OH production in isoprene ozonolysis (reactions 5–8):



Previous quantum chemical and RRKM/master equation simulations of isoprene ozonolysis by Zhang<sup>40,41</sup> and by our laboratory<sup>42</sup> have indicated that, in order for predicted •OH yields to agree with the experimental consensus of Atkinson,<sup>43</sup> Paulson,<sup>44</sup> Neeb,<sup>45</sup> and Malkin et al.,<sup>46</sup> it is necessary to assume that all of the thermalized *syn*-methyl CI isomerizes and decomposes to afford •OH. The TST results reported here confirm the validity of this assumption.

## II. Computational Methods

**A. Electronic Structure Calculations.** The geometries of all stationary points considered in this paper were optimized at the QCISD level of theory. The acetaldehyde oxide isomerization and decomposition reactions were treated with both the 6-31G(d) basis set and Truhlar's MG3<sup>47,48</sup> (or 6-311++G(2df,2p)) basis set, whereas larger systems were treated only with 6-31G(d). QCISD/6-31G(d) harmonic frequencies were computed for all structures. Each reported minimum had all real frequencies, and each reported transition structure had one imaginary frequency. We determined the minima associated with each transition structure by animation of the imaginary frequency. Truhlar and co-workers<sup>49,50</sup> have shown that QCISD/MG3 predicts accurate transition structure geometries and have developed barrier height benchmark databases based upon this model chemistry's geometries.<sup>51,52</sup> Radom and co-workers<sup>53–55</sup> have found that relative energies based on QCISD/6-31G(d) geometries are usually very accurate.

Electronic energies of all stationary points were calculated using the multicoefficient G3 (MCG3) method employing Lynch and Truhlar's<sup>56</sup> version 3m parameters. MCG3 has been shown to predict highly accurate energetics for covalent bond thermochemistry, noncovalent interactions, and hydrogen transfer barrier heights.<sup>49,56,57</sup>

For the variational transition state theory calculations described below, it was necessary to employ a more affordable, but still relatively accurate, model chemistry to calculate partition functions along the reactions' minimum energy paths. We tested three density functional theory (DFT) methods, B3LYP,<sup>58–60</sup> MPW1K,<sup>61</sup> and B3P86,<sup>62</sup> against the MCG3//QCISD predictions. All DFT calculations employed the 6-31+G(d,p) basis set.<sup>63–65</sup> Although B3LYP underestimates the barriers to hydrogen-atom transfer reactions in open shell systems,<sup>50,61,66–69</sup> this systematic error may not affect predictions for the closed-shell<sup>70</sup> carbonyl oxides considered here.<sup>20</sup> For MPW1K and B3P86, Truhlar and co-workers<sup>61,62</sup> optimized the fraction of Hartree–Fock exchange to reproduce accurately known barrier heights for hydrogen transfer reactions involving radicals.

Most of the quantum chemistry calculations were carried out using the Gaussian 03 program suite.<sup>71</sup> MCG3 calculations were performed using MULTILEVEL.<sup>72</sup> The Supporting Information reports the coordinates, electronic energy, and zero-point vibrational energy for all stationary points considered in this paper.

**B. RRKM/Master Equation Calculations.** We used Version 2008.3 of Barker's MultiWell program suite<sup>73,74</sup> to solve the master equation for the cyclereversion of *trans*-2-butene and for the isomerization of the resulting *syn* and *anti* acetaldehyde oxide. The relative electronic energies of all participating species were taken from MCG3 calculations based on either QCISD/6-31G(d) optimized geometries (for the *trans*-2-butene primary ozonide simulations) or QCISD/MG3 optimized geometries (for the acetaldehyde oxide simulations). All zero-point energy corrections were based on QCISD/6-31G(d) harmonic vibrational frequencies scaled by 0.9776, as recommended by Scott and Radom.<sup>75</sup> Microcanonical rate constants  $k(E)$  were computed using Rice–Ramsperger–Kassel–Marcus (RRKM) theory,<sup>76</sup> with the required sums and densities of states being calculated based on either QCISD/MG3 or QCISD/6-31G(d) optimized geometries and on QCISD/6-31G(d) frequencies. For the primary ozonide simulations, the active *K*-rotor contribution to the sums and densities of states was restricted by a total angular momentum quantum number of  $J = 44$  at 300 K.<sup>9,77,78</sup> In the



master equation simulations, we did not treat low-frequency internal rotations as hindered rotors.

We treated collisional stabilization with the exponential-down model, using an energy grain size of  $10\text{ cm}^{-1}$  and assuming an average energy transferred per deactivating collision ( $\langle E_d \rangle$ ) of  $300\text{ cm}^{-1}$ .<sup>79</sup> The bath gas was  $\text{N}_2$  at 298 K, with Lennard-Jones parameters of  $\sigma = 3.74\text{ \AA}$  and  $\epsilon = 82\text{ K}$ .<sup>80,81</sup> Following the same procedures<sup>82–85</sup> used in our study of isoprene ozonolysis,<sup>42</sup> we estimated Lennard-Jones parameters of  $\sigma = 6.54\text{ \AA}$  and  $\epsilon = 382\text{ K}$  for the primary ozonide and parameters of  $\sigma = 5.39\text{ \AA}$  and  $\epsilon = 423\text{ K}$  for acetaldehyde oxide.

Each simulation was run for  $10^3$  collisions to ensure that the pseudo steady state<sup>86</sup> was achieved. Trials were run at pressures of 1, 10, 50, 100, 200, 300, 400, 500, 600, 700, and 760 Torr. Each pseudo steady-state yield reported is the average result of  $10^5$  Monte Carlo simulations. For a yield of  $\sim 100\%$ , the statistical uncertainty is no higher than  $\pm 0.2\%$ . For a yield of  $\sim 1\%$ , the statistical uncertainty is no higher than  $\pm 0.04\%$ . Details of how the initial energy distribution was represented in a given simulation are given in the Results and Discussion section below.

**C. Transition State Theory Calculations.** We computed thermal rate constants for reactions 1–8 above using canonical variational transition state theory (CVT)<sup>87–89</sup> as implemented in Truhlar’s POLYRATE 9.1<sup>90</sup> and GAUSSRATE 9.1,<sup>91</sup> the latter being used to interface POLYRATE 9.1 with Gaussian 03 for the electronic structure calculations. Partition functions along the minimum energy path were computed with the B3LYP/6-31+G(d,p) model chemistry. Vibrational modes greater than  $200\text{ cm}^{-1}$  were treated as harmonic oscillators and scaled by 0.9806. Vibrational modes less than  $200\text{ cm}^{-1}$  were treated as hindered internal rotors, following the method of Chuang and Truhlar.<sup>92</sup> Reaction barriers were determined with MCG3//QCISD/MG3 calculations for acetaldehyde oxide reactions and MCG3//QCISD/6-31G(d) calculations for methyl vinyl carbonyl oxide reactions.

Our quantum chemical data (presented in Tables 2 and 3 below) support the assumption that the rate of decomposition of the prereactive complexes **8**, **8 $\alpha$** , **8 $\beta$** , and **11** (that is, the reverse of reactions 3a, 4a, 6a, and 8a) is much faster than the rate of addition of water across the carbonyl oxide 1,3-dipole (reactions 3b, 4b, 6b, and 8b). Hence, following the treatment of Vivier-Bunge and co-workers,<sup>93,94</sup> we compute the overall rate constant for each hydration reaction  $i$  thus:

$$k_i = K_{\text{eq},i\alpha} k_{\text{fb}}, \text{ where } i = 3, 4, 6, \text{ or } 8 \quad (9)$$

Equilibrium constants  $K_{\text{eq},i\alpha}$  for the complex formation reactions were calculated based on B3LYP/6-31+G(d,p) partition functions and either MCG3//QCISD/MG3 energies (for the acetaldehyde oxide complexes) or MCG3//QCISD/6-31G(d) energies (for the methyl vinyl carbonyl oxide complexes). Again, vibrational modes greater than  $200\text{ cm}^{-1}$  were treated as harmonic oscillators and were scaled by 0.9806, whereas vibrational modes less than  $200\text{ cm}^{-1}$  were treated as hindered internal rotors.<sup>92</sup>

We estimated the impact of tunneling on all thermal rate constants using the asymmetric Eckart potential.<sup>95,96</sup> Eckart transmission coefficients depend on the reaction barrier, reaction energy, and the magnitude of the imaginary frequency,  $\nu^*$ , of the vibration along the reaction coordinate. We used MCG3//QCISD energetics (with the basis set again depending on the size of the system) and B3LYP/6-31+G(d,p) frequencies in our calculations. In our previous work<sup>69</sup> on the 1,4-hydrogen shift

within the 2-hydroxyethoxy radical, we found that between 200 and 298 K the Eckart model predicts transmission coefficients 1–3 orders of magnitude higher than the highly rigorous microcanonical optimized multidimensional tunneling ( $\mu\text{OMT}$ )<sup>97</sup> method. However, the transition structure for the 1,4-hydrogen shift has a BB1K/6-31+G(d,p) imaginary frequency of  $3295i\text{ cm}^{-1}$ . The transition structure for the 1,4-hydrogen shift in *syn* acetaldehyde oxide, in contrast, has a B3LYP/6-31+G(d,p) imaginary frequency of  $1601i\text{ cm}^{-1}$ . The lower magnitude of the imaginary frequency reflects a wider adiabatic potential, which in turn will lead to lower transmission coefficients. In such a situation, the Eckart model may be not nearly as inaccurate. We tested this notion by comparing the predictions of the Eckart method to those of Truhlar’s small-curvature tunneling (SCT),<sup>98</sup> version-4 large-curvature tunneling (LCT),<sup>99</sup> and microcanonical optimized multidimensional tunneling ( $\mu\text{OMT}$ )<sup>97</sup> methods for the 1,4-hydrogen shift in *syn* acetaldehyde oxide. Convergence of the transmission coefficients to three significant figures required computation of the minimum energy path from  $s = -1.2 a_0$  to  $s = +2.5 a_0$ , with a step size of  $0.0005 a_0$  and Hessians being computed every five steps. For the sake of computational efficiency, the comparison was based solely on B3LYP/6-31+G(d,p) electronic structure data.

**D. Falloff Curve Calculations.** We used Gilbert’s UNIMOL program suite<sup>100</sup> to estimate the falloff curves for the 1,4-hydrogen shift reactions for the three *syn*-methyl CIs considered here (reactions 1, 5, and 7). In all cases, vibrational energy levels were determined from QCISD/6-31G(d) frequency calculations. Rotational energy levels were determined from QCISD/MG3 optimized geometries for acetaldehyde oxide and from QCISD/6-31G(d) optimized geometries for the methyl vinyl carbonyl oxides. Reaction barriers were determined from MCG3//QCISD/MG3 calculations for acetaldehyde oxide and from MCG3//QCISD/6-31G(d) calculations for the methyl vinyl carbonyl oxides. As in the MultiWell calculations, we used the exponential-down model for collisional stabilization and assumed the average energy transferred per deactivating collision to be  $300\text{ cm}^{-1}$ . For the acetaldehyde oxide simulations, we used the same Lennard-Jones parameters described above in Section B. For the methyl vinyl carbonyl oxide simulations, we used the parameters we estimated previously<sup>42</sup> of  $\sigma = 6.29\text{ \AA}$  and  $\epsilon = 358\text{ K}$ . To incorporate both variational and tunneling effects on the rate constant, we adjusted the reaction barrier so that the high-pressure limit TST rate constant calculated by UNIMOL matched our best estimate of the rate constant at a given temperature (200, 250, or 298 K). This approach, while highly approximate, will not affect the validity of the qualitative conclusions we draw below.

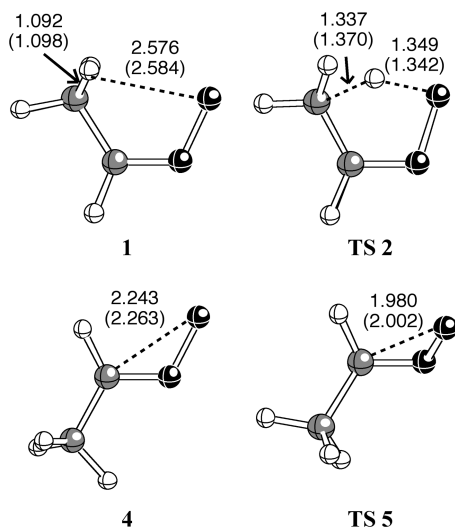
### III. Results and Discussion

**A. Quantum Chemistry.** Table 1 summarizes our predictions of the energetics of reactions 1 and 2. As we have reported

**TABLE 1: Zero-Point Corrected Relative Energies (0 K, kcal mol<sup>-1</sup>) for Reactions 1 and 2**

model chemistry	relative to <b>1</b>		relative to <b>4</b>	
	TS 2	3	TS 5	6
B3LYP/6-31+G(d,p)	16.74	−15.96	16.89	−19.91
MPW1K/6-31+G(d,p)	16.32	−19.14	17.35	−26.43
BB1K/6-31+G(d,p)	16.43	−18.69	17.55	−28.21
MCG3//QCISD/6-31G(d) <sup>a</sup>	17.34	−18.07	16.33	−23.99
MCG3//QCISD/MG3 <sup>a</sup>	17.91	−17.62	15.40	−23.44

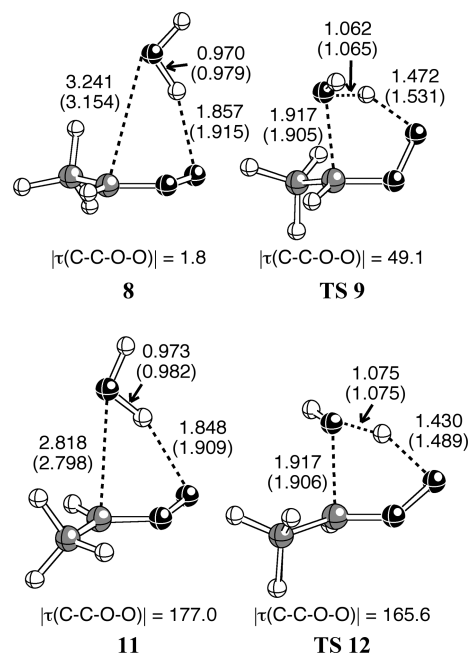
<sup>a</sup> Zero-point energies based on B3LYP/6-31+G(d,p) harmonic frequencies scaled by 0.9806.



**Figure 1.** QCISD-optimized geometries of the reactants and transition structures for reactions 1 and 2. (Gray represents carbon, black represents oxygen, and white represents hydrogen.) Interatomic distances (in Å) obtained with the MG3 and the 6-31G(d) basis sets; the latter predictions are in parentheses.

earlier,<sup>20</sup> B3LYP is *not* systematically worse than the more contemporary MPW1K and BB1K density functionals in predicting the barriers for hydrogen atom transfers in closed-shell systems. In fact, the B3LYP/6-31+G(d,p) barriers for reactions 1 and 2 are the closest to the high-level MCG3//QCISD/MG3 barrier. However, all three density functional theory methods underestimate the barrier to reaction 1 and overestimate the barrier to reaction 2. Compared to MCG3//QCISD/MG3, the MCG3//QCISD/6-31G(d) model chemistry also predicts a lower barrier for reaction 1 and a higher barrier for reaction 2. These differences may be partially rationalized by the optimized geometries shown in Figure 1. The MG3 basis set predicts that at **TS 2**,  $R(\text{C}-\text{H})$  has been lengthened by 0.245 Å and  $R(\text{H}-\text{O})$  has been shortened by 1.227 Å. The 6-31G(d) basis set predicts that  $R(\text{C}-\text{H})$  has been lengthened by 0.272 Å and  $R(\text{H}-\text{O})$  has been shortened by 1.242 Å. Clearly, the QCISD/MG3 geometry for **TS2** is earlier than the QCISD/6-31G(d) geometry. This is consistent with a higher MCG3//QCISD/MG3 barrier for the exothermic reaction 1. For reaction 2, no simple explanation based on the Hammond postulate<sup>101</sup> can be made. However, it is the case that the distance between the reacting C and O atoms is  $\sim 0.02$  Å shorter in both **4** and **TS 5** with the MG3 basis set.

Table 2 summarizes our predictions of the energetics for reactions 3 and 4, and compares them with the predictions of Ryzhkov and Ariya.<sup>29</sup> It is clear that B3LYP is far more accurate, as judged by agreement with the MCG3 predictions,



**Figure 2.** QCISD-optimized geometries of the reactants and transition structures for reactions 3b and 4b. Interatomic distances (in Å) obtained with the MG3 and the 6-31G(d) basis sets; the latter predictions are in parentheses. Torsional angles (in deg) obtained with the MG3 basis set.

than MPW1K and BB1K for both minima and transition structures. In addition, the agreement between MCG3 energies based on QCISD/6-31G(d) and QCISD/MG3 geometries is significantly better than for reactions 1 and 2. This is in spite of disagreements in predicted interatomic distances for the complexes (**8** and **11**) and the transition structures (**TS 9** and **TS 12**) as large as 0.06 Å, as Figure 2 illustrates. This reflects the relative flatness of the potential energy surface in the vicinity of these stationary points.

Table 2 reveals a substantial difference in the barriers for the hydration of *syn* versus *anti* acetaldehyde oxide. The 6 kcal mol<sup>-1</sup> difference in reaction barrier, as we shall see, dramatically differentiates the atmospheric fates of the *syn* and *anti* forms. Part of the difference may be attributed to geometrical factors (see Figure 2). In minimum **8**, water complexation has only weakly perturbed the *syn*-methyl CI; the C-C-O-O moiety is less than 2° from planarity. However, in transition structure **TS 9**, the water is significantly closer to the carbonyl oxide than in **8**. To minimize steric repulsion, the peroxy bond in **TS 9** must swing substantially out of the C-C-O plane; the magnitude of the C-C-O-O dihedral angle is 49.1°. This perturbation in geometry deprives the *syn*-methyl CI of its aromatic-like 6 $\pi$ -electron stabilization.<sup>102–104</sup> In contrast, the *anti*-methyl CI does not benefit from 6 $\pi$ -electron stabilization,

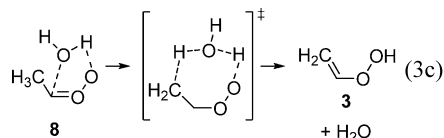
**TABLE 2: Zero-Point Corrected Relative Energies (0 K, kcal mol<sup>-1</sup>) for Reactions 3 and 4**

model chemistry	relative to <b>1</b> + <b>7</b>			relative to <b>4</b> + <b>7</b>		
	<b>8</b>	<b>TS 9</b>	<b>10</b>	<b>11</b>	<b>TS 12</b>	<b>10</b>
B3LYP/6-31+G(d,p)	-7.00	6.24	-32.28	-7.82	0.99	-36.13
MPW1K/6-31+G(d,p)	-9.54	2.65	-43.47	-8.95	-1.01	-45.92
BB1K/6-31+G(d,p)	-7.23	5.51	-39.12	-8.33	0.25	-43.43
MCG3//QCISD/6-31G(d) <sup>a</sup>	-6.51	8.61	-35.08	-7.56	2.79	-38.52
MCG3//QCISD/MG3 <sup>a</sup>	-6.22	8.83	-34.64	-7.57	2.91	-38.12
CCSD(T)/6-311+G(2d,2p) <sup>b</sup>	-7.5	7.0	-38.3	-8.8	0.6	-42.8

<sup>a</sup> Zero-point energies based on B3LYP/6-31+G(d,p) harmonic frequencies scaled by 0.9806. <sup>b</sup> Based on B3LYP/6-311+G(2d,2p) optimized geometries and harmonic frequencies, as well as basis set superposition error corrections for the relative energies of **8** and **11**. Taken from Ryzhkov and Ariya.<sup>29</sup>

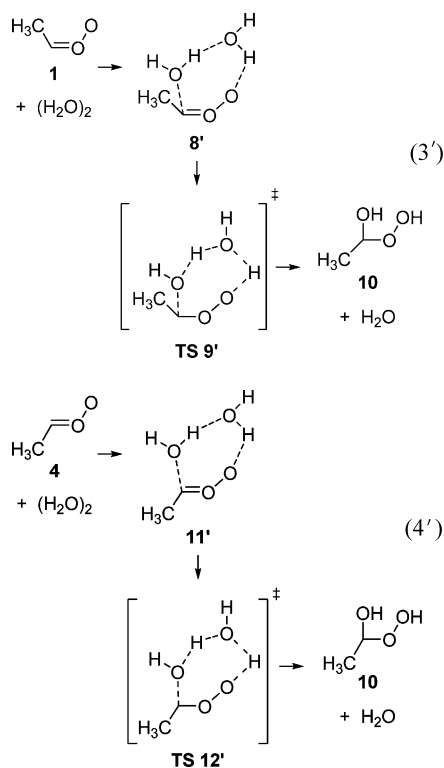
which makes the distortion of the CI upon water complexation considerably less costly energetically.

Anglada and co-workers<sup>27,105</sup> have presented computational evidence that complex **8** can also react to form the labile vinyl hydroperoxide **3** and H<sub>2</sub>O:



This implies that hydration of the *syn*-alkyl CI would not necessarily inhibit •OH formation. Since the barrier for reaction 3c is predicted<sup>27</sup> to be 3–4 kcal mol<sup>−1</sup> higher than the barriers for reaction 3b, we neglected consideration of reaction 3c in this study. However, very recent work by Tillmann et al.<sup>106</sup> indicates that the •OH yield from α-pinene ozonolysis increases with increasing RH. It may be that the analog of reaction 3c for the α-pinene-derived CI may have a barrier lower than the barrier for the analog of reaction 3b.

Ryzhkov and Ariya<sup>29</sup> performed CCSD(T)/6-311+G(2d,2p)//B3LYP/6-311+G(2d,2p) calculations on both reactions 3 and 4 above and the analogous reactions (3' and 4') involving water dimer:



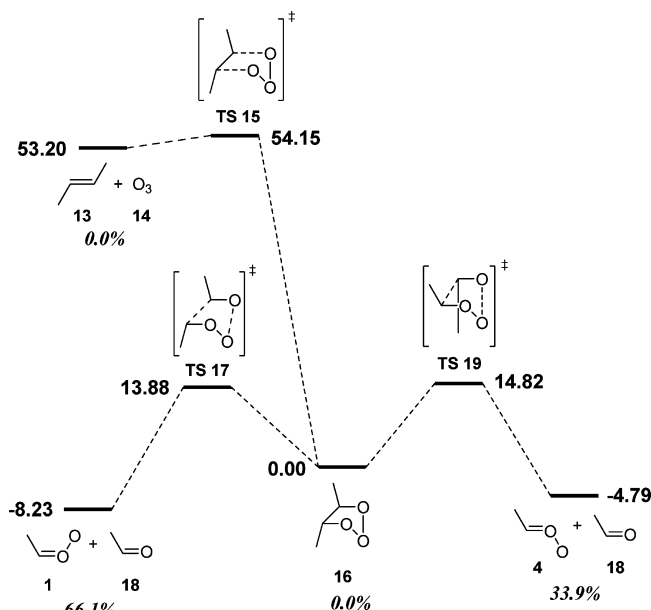
For the monomer reactions, Table 2 indicates that the CCSD(T)/6-311+G(2d,2p) barriers are ~2 kcal mol<sup>−1</sup> lower than our most accurate estimates. This discrepancy leads to significantly different CVT rate constants, as we shall consider below.

Finally, Table 3 presents our MCG3//QCISD/6-31G(d) predictions for reactions 5–8. The barriers for the reactions of **1α** are 1–2 kcal mol<sup>−1</sup> lower in energy than the barriers for the reactions of **1β**. The prediction that conformer **1α** is significantly more reactive than conformer **1β** agrees with

**TABLE 3: Zero-Point Corrected Relative Energies (0 K, kcal mol<sup>−1</sup>) for Reactions 5–8<sup>a</sup>**

system	relative to <b>1x</b>		relative to <b>1x</b> + <b>7</b>		
	TS <b>2x</b>	<b>3x</b>	<b>8x</b>	TS <b>9x</b>	<b>10x</b>
<b>x</b> = <b>α</b>	16.86	−16.48	−6.88	7.65	−30.26
<b>x</b> = <b>β</b>	18.34	−12.12	−6.09	9.82	−28.30

<sup>a</sup> Electronic energies from MCG3//QCISD/6-31G(d) calculations; zero-point energies based on B3LYP/6-31+G(d,p) harmonic frequencies scaled by 0.9806.

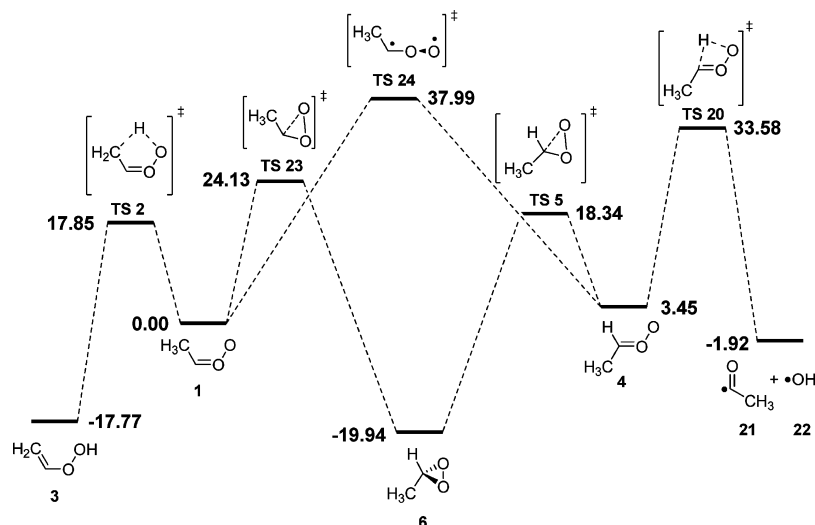


**Figure 3.** *Trans*-2-butene ozonolysis mechanism treated by RRKM/master equation simulations. The MCG3//QCISD/6-31G(d) relative energies (at 0 K, in kcal mol<sup>−1</sup>) are given in bold font, and the 1 atm pseudo steady-state yields for the well and exit channels are given in bold italic font.

previous quantum chemical predictions by Zhang and Zhang,<sup>40</sup> Aplincourt and Anglada,<sup>105</sup> and our laboratory.<sup>42</sup>

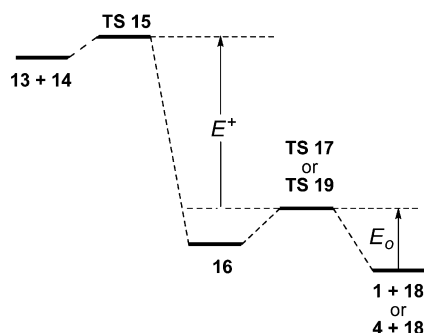
**B. Master Equation Simulations.** Figure 3 presents the mechanism considered in our simulations of the formation and cycloreversion of the *trans*-2-butene primary ozonide. The formation of the primary ozonide (**16**) was the entrance channel, and the initial energy of **16** was represented by a shifted thermal (298 K) distribution<sup>107</sup> truncated at the zero-point-corrected energy of transition structure **TS 15**. The exit channels were the formation of *syn* acetaldehyde oxide **1** (and acetaldehyde, **18**), formation of *anti* acetaldehyde oxide **4** (and acetaldehyde, **18**), and reversion to *trans*-2-butene (**13**) and ozone (**14**). There was no statistically significant variation in pseudo steady-state yields (shown in Figure 3) from 1 Torr up to 1 atm. None of **16** is predicted either to revert to reactants or to be collisionally stabilized. A large majority (66%) of **16** decomposes to the *syn* conformer of the CI. The preference for the *syn* conformer arises both from the 0.9 kcal mol<sup>−1</sup> lower barrier to its formation and from the number of states available to the chemically activated **16** at the *syn* transition state (**TS 17**), particularly from the active *K*-rotor of **TS 17**. Our results are consistent with the *trans*-2-butene primary ozonide simulations of Marston and co-workers,<sup>108</sup> who used MP2/6-31G(d) and RRK calculations to estimate a yield for **1** of 75%.

Figure 4 presents the mechanism considered in our simulations of acetaldehyde oxide chemistry. In principle, both conformers can form **22**, the *syn* conformer via the labile vinyl



**Figure 4.** Acetaldehyde oxide mechanism treated by RRKM/master equation simulations. The MCG3//QCISD/MG3 relative energies (at 0 K, in kcal mol<sup>-1</sup>) are shown.

### SCHEME 3: Energy Partitioning in Ozonolysis



hydroperoxide **3** (see Scheme 2 above), and the *anti* conformer directly via a 1,3-hydrogen shift transition structure (TS **20**). Similarly, both conformers can close (via transition structures TS **5** and TS **23**) to methyl dioxirane (**6**). Finally, the two conformers can interconvert. As previously found by Anglada et al.<sup>14</sup> the lowest energy interconversion pathway involves rotation about the C=O double bond (via singlet diradical transition structure TS **24**).

We performed two sets of simulations, one set with the *syn* CI as the entrance channel, and the other set with the *anti* CI as the entrance channel. Equation 10 describes the initial energy distribution of CI **Y**,  $f^Y(E)$  (where **Y** = **1** or **4**), used in the simulations, with key energetic parameters defined in Scheme 3:

$$f^Y(E) = \frac{\rho_Y(E)W_{18}(E^+ - E)}{\int_0^{E^+} \rho_Y(\varepsilon)W_{18}(E^+ - \varepsilon)d\varepsilon} \quad (10)$$

This approach, due to Forst<sup>107,109</sup> and first applied to ozonolysis simulations by Cremer and co-workers,<sup>9</sup> assumes the following: (1) The maximum internal energy,  $E^+$ , available to a given CI conformer is the difference in the energies of the cycloaddition transition structure (TS **15**, Figure 3) and the cycloreversion transition structure leading to that conformer (TS **17** or TS **19**, Figure 3). (2) The potential energy released in the exit channel,  $E_o$ , goes entirely into the relative translation of products **1** + **18** or **4** + **18**. (3) There is a statistical partitioning of  $E^+$  based on the density of states of the given acetaldehyde oxide ( $\rho_1$  or  $\rho_4$ ) and the sum of states of the co-generated

acetaldehyde ( $W_{18}$ ). Although there are examples in the literature where this statistical treatment is manifestly inaccurate,<sup>110</sup> molecular dynamics simulations by Hase and co-workers<sup>111</sup> confirm the validity of all three of the above assumptions when describing the initial energy distribution of the acetaldehyde oxide formed in propene ozonolysis. The consistency of our master equation predictions with available experimental data (discussed in Section D below) also validates these assumptions to some extent. We nevertheless acknowledge that the CIs' initial energy distribution is probably the greatest source of uncertainty in our work.

Pseudo steady-state yields as a function of bath gas pressure are reported in Tables 4 and 5. For *syn* acetaldehyde oxide (Table 4), the dominant isomerization pathway is the 1,4-hydrogen shift to vinyl hydroperoxide **3**, with only 1–2% of

**TABLE 4: Master Equation Percent Yields for *Syn* Acetaldehyde Oxide (see Figure 4)**

torr	species <b>1</b>	species <b>3</b>	species <b>4</b>	species <b>6</b>	species <b>21</b> + <b>22</b>
1	26.9	71.2	0.0	1.9	0.0
10	32.3	65.8	0.0	1.9	0.0
50	41.9	56.2	0.0	1.9	0.0
100	47.4	50.8	0.0	1.8	0.0
200	54.1	44.2	0.0	1.7	0.0
300	58.7	39.5	0.0	1.8	0.0
400	61.9	36.5	0.0	1.6	0.0
500	64.7	33.7	0.0	1.6	0.0
600	66.5	32.0	0.0	1.5	0.0
700	68.0	30.5	0.0	1.5	0.0
760	69.2	29.3	0.0	1.5	0.0

**TABLE 5: Master Equation Percent Yields for *Anti* Acetaldehyde Oxide (see Figure 4)**

torr	species <b>1</b>	species <b>3</b>	species <b>4</b>	species <b>6</b>	species <b>21</b> + <b>22</b>
1	0.0	0.0	29.0	71.0	0.0
10	0.0	0.0	33.9	66.1	0.0
50	0.0	0.0	40.8	59.2	0.0
100	0.0	0.0	44.9	55.1	0.0
200	0.0	0.0	50.3	49.7	0.0
300	0.0	0.0	53.3	46.7	0.0
400	0.0	0.0	55.9	44.1	0.0
500	0.0	0.0	58.0	42.0	0.0
600	0.0	0.0	59.8	40.2	0.0
700	0.0	0.0	61.1	38.9	0.0
760	0.0	0.0	62.0	38.0	0.0



**TABLE 6: Tunneling Results for the 1,4-Hydrogen Shift in *Syn* Acetaldehyde Oxide**

<i>T</i> (K)	transmission coefficient				% error <sup>a</sup>
	SCT	LCT	$\mu$ OMT	Eckart	
200	$1.18 \times 10^6$	$4.30 \times 10^1$	$1.79 \times 10^6$	$3.54 \times 10^5$	−80.2
250	$2.18 \times 10^3$	$4.30 \times 10^0$	$2.39 \times 10^3$	$9.48 \times 10^2$	−60.3
298	$8.92 \times 10^1$	$1.55 \times 10^0$	$9.06 \times 10^1$	$5.50 \times 10^1$	−39.3

<sup>a</sup> Based on the deviation of the Eckart prediction from the  $\mu$ OMT prediction.

the reactant isomerizing to dioxirane **6**. None of the *syn* conformer isomerizes to the *anti* conformer. We predict a substantial pressure dependence. Up to 100 Torr, a majority of the CI should isomerize, but at 1 atm, almost 70% of the CI is predicted to be collisionally stabilized. Assuming that the yield of **3** is a surrogate for the yield of  $\bullet$ OH, our simulations predict a substantial pressure dependence for  $\bullet$ OH formation on the prompt time scale. This is consistent with Kroll et al.'s LIF measurements of  $\bullet$ OH from *trans*-2-butene ozonolysis.<sup>112</sup>

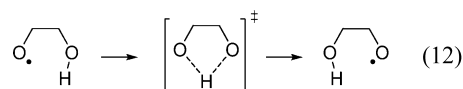
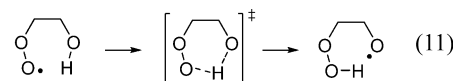
For *anti* acetaldehyde oxide (Table 5), the exclusive isomerization pathway is closure to dioxirane **6**; none of the *anti* conformer isomerizes to the *syn* conformer or decomposes to formyl (**21**) and hydroxyl (**22**) radicals. As with the *syn* form, we predict a significant pressure dependence, with a majority of CI isomerizing up to 100 Torr, but collisional stabilization dominating at higher pressures.

Our results for both conformers of acetaldehyde oxide are in agreement with those reported by Kroll et al.<sup>10</sup> based on B3LYP energetics, geometries, and frequencies. Both studies predict that ~25% of the *syn* CI is formed vibrationally cold, and that an additional 50% of the *syn* CI is collisionally stabilized as bath gas pressure is increased to 1 atm. Both studies predict similar trends for the *anti* CI, although we predict a ~10% lower yield of dioxirane at all pressures.

Given that a large majority of the CI formed in *trans*-2-butene ozonolysis is collisionally stabilized at atmospheric pressure, the product distribution of the ozonolysis reaction will be largely determined by thermal rate constants. We next turn to our predictions of these rate constants.

**C. Transition State Theory Calculations.** Table 6 presents transmission coefficients predicted for reaction 1 at atmospherically relevant temperatures using a variety of semiclassical methods. Of the tunneling methods employed here, the  $\mu$ OMT method's predictions agree best with fully quantal calculations,<sup>113,114</sup> and we will accept the  $\mu$ OMT results as the accurate values. The fact that the  $\mu$ OMT coefficients are slightly larger than the SCT coefficients indicates that large-curvature tunneling makes a non-negligible contribution to the overall tunneling mechanism.

As compared to the  $\mu$ OMT method, the simplistic Eckart method systematically underestimates transmission coefficients, with errors as large as −80% at 200 K. However, these errors are relatively modest compared to the errors we have found for other intramolecular hydrogen transfer reactions<sup>69</sup> (reactions 11 and 12):



For reaction 11, the Eckart method predicted a 200 K transmission coefficient 330% higher than the  $\mu$ OMT method. For reaction 12, the Eckart method predicted a 200 K transmission coefficient 4 orders of magnitude higher than the  $\mu$ OMT method. Hence, the Eckart method is far better for the reactions under consideration here. Moreover, for the chemical questions we were asking, we decided that using a somewhat inaccurate tunneling method was worth the gain in computational efficiency.

Table 7 summarizes our prediction of CVT rate constants and Eckart transmission coefficients for all of the unimolecular reactions considered in this paper. Variational optimization of the transition state had virtually no impact on the rate constants for the 1,4-hydrogen shift (reactions 1, 5, and 7) or for ring closure (reaction 2); the nonvariational rate constants (not shown) agree with the variational rate constants to two or three

**TABLE 7: Variational Transition State Theory Results for Unimolecular Reactions**

reaction	CVT rate constant (s <sup>−1</sup> )			transmission coefficient		
	200 K	250 K	298 K	200 K	250 K	298 K
1,4-H shift						
reaction 1	$1.30 \times 10^{-7}$	$1.13 \times 10^{-3}$	$3.88 \times 10^{-1}$	$7.47 \times 10^5$	$1.31 \times 10^3$	$6.25 \times 10^1$
reaction 5	$1.84 \times 10^{-6}$	$9.46 \times 10^{-3}$	$2.32 \times 10^0$	$4.99 \times 10^5$	$1.19 \times 10^3$	$6.31 \times 10^1$
reaction 7	$4.89 \times 10^{-8}$	$5.33 \times 10^{-4}$	$2.14 \times 10^{-1}$	$1.02 \times 10^6$	$1.55 \times 10^3$	$6.88 \times 10^1$
ring closure						
reaction 2	$1.23 \times 10^{-4}$	$3.32 \times 10^{-1}$	$5.43 \times 10^1$	$1.64 \times 10^0$	$1.36 \times 10^0$	$1.24 \times 10^0$
hydration						
reaction 3b	$1.06 \times 10^{-5}$	$1.86 \times 10^{-2}$	$2.21 \times 10^0$ ( $1.31 \times 10^1$ ) <sup>a</sup> ( $3.67 \times 10^2$ ) <sup>b</sup>	$1.99 \times 10^0$	$1.52 \times 10^0$	$1.34 \times 10^0$
reaction 4b	$6.30 \times 10^{-1}$	$1.16 \times 10^2$	$3.20 \times 10^3$ ( $4.97 \times 10^5$ ) <sup>a</sup> ( $1.04 \times 10^6$ ) <sup>b</sup>	$2.17 \times 10^0$	$1.61 \times 10^0$	$1.39 \times 10^0$
reaction 6b	$1.07 \times 10^{-5}$	$1.57 \times 10^{-2}$	$1.64 \times 10^0$ ( $8.80 \times 10^0$ ) <sup>c</sup>	$6.60 \times 10^0$	$2.86 \times 10^0$	$2.01 \times 10^0$
reaction 8b	$5.62 \times 10^{-7}$	$1.64 \times 10^{-3}$	$2.70 \times 10^{-1}$ ( $1.44 \times 10^0$ ) <sup>c</sup>	$1.87 \times 10^1$	$4.51 \times 10^0$	$2.64 \times 10^0$

<sup>a</sup> From Anglada et al.;<sup>27</sup> based on CCSD(T)/6-311+G(2d,2p)//B3LYP/6-311+G(2d,2p) energies and B3LYP/6-31G(d,p) partition functions.

<sup>b</sup> From Ryzhkov and Ariya;<sup>29</sup> based on CCSD(T)/6-311+G(2d,2p)//B3LYP/6-311+G(2d,2p) energies and B3LYP/6-311+G(2d,2p) partition functions. <sup>c</sup> From Aplincourt and Anglada;<sup>105</sup> based on G2M-RCC5//B3LYP/6-311+G(2d,2p) energies and B3LYP/6-31G(d,p) partition functions.

**TABLE 8: Equilibrium Constants (cm<sup>3</sup> molecule<sup>-1</sup>) for Complex Formation Reactions**

reaction	reactant	product	200 K	250 K	298 K
3a	<b>1</b>	<b>8</b>	$4.92 \times 10^{-19}$	$1.91 \times 10^{-20}$	$2.45 \times 10^{-21}$
4a	<b>4</b>	<b>11</b>	$3.56 \times 10^{-17}$	$7.43 \times 10^{-19}$	$6.46 \times 10^{-20}$
6a	<b>1<math>\alpha</math></b>	<b>8<math>\alpha</math></b>	$3.32 \times 10^{-18}$	$9.72 \times 10^{-20}$	$1.04 \times 10^{-20}$
8a	<b>1<math>\beta</math></b>	<b>8<math>\beta</math></b>	$3.92 \times 10^{-19}$	$1.68 \times 10^{-20}$	$2.28 \times 10^{-21}$

significant figures. For addition of water across the 1,3-dipole (reactions 3b, 4b, 6b, and 8b), the variational rate constants are 20–30% lower than the nonvariational rate constants (not shown). As expected, tunneling will have the largest impact on the rate of the 1,4-hydrogen shift. At 200 K, the Eckart model predicts transmission coefficients on the order of  $10^5$  to  $10^6$ . Moreover, our validation study discussed above suggests the actual transmission coefficients may be slightly higher. The rate constants for both the 1,4-hydrogen shift and hydration are larger for *syn*-methyl vinyl CI **1 $\alpha$**  than for CI **1 $\beta$** . This is consistent with the MCG3//QCISD/6-31G(d) energetics reported in Table 3.

Table 7 also reports nonvariational TST rate constants previously predicted by Anglada and co-workers for the hydration reactions.<sup>27,105</sup> Our predictions are within a factor of 6 of the previous predictions for every reaction except for 4b, for which we predict a rate constant 2 orders of magnitude lower than do Anglada et al.<sup>27</sup> This is clearly a consequence of different quantum chemical predictions. Table 2 indicates that the barrier for reaction 4b is 10.5 kcal mol<sup>-1</sup> at our highest level of theory, MCG3//QCISD/MG3. Anglada et al.<sup>27</sup> report a CCSD(T)/6-311+G(2d,2p)//B3LYP/6-311+G(2d,2p) barrier for reaction 4b of 7.4 kcal mol<sup>-1</sup>. We have demonstrated in previous work<sup>28,115</sup> that composite methods can predict more accurate energetics for peroxy species than CCSD(T) single-point calculations with polarized triple- $\zeta$  basis sets.<sup>27,116,117</sup> We are therefore confident in the accuracy of the rate constant we have predicted for reaction 4b. For the same reason, it is likely that the CVT rate constants predicted by Ryzhkov and Ariya<sup>29</sup> for water monomer reactions 3b and 4b overestimate the true values.

Table 8 reports the equilibrium constants for the formation of the CI-water complexes (reactions 3a, 4a, 6a, and 8a). At 200 K, complexation of *anti* acetaldehyde oxide **4** is significantly more favorable thermodynamically than complexation of any of the *syn*-methyl carbonyl oxides (**1**, **1 $\alpha$** , or **1 $\beta$** ), reflecting the greater exothermicity in forming complex **11** than in forming complexes **8**, **8 $\alpha$** , or **8 $\beta$**  (Tables 2 and 3). For the same reason, while the equilibrium constants for the formation of **8**, **8 $\alpha$** , and **8 $\beta$**  decrease by around 2 orders of magnitude from 200 to 298 K, the equilibrium constant for the formation of **11** decreases by almost 3 orders of magnitude.

As shown in Tables 2 and 3, the energy required to decompose any of these complexes back to CI and H<sub>2</sub>O is at least 3 kcal mol<sup>-1</sup> less than the activation barrier for the formation of the  $\alpha$ -hydroxy hydroperoxide. Moreover, extensive searching of the potential energy surface did not reveal any transition structure for any of complexation reactions, in agreement with the previous work of Anglada and co-workers.<sup>27,105</sup> These findings support the contention that CI hydration involves an equilibrium between the reactants and the prereactive complex (reactions 3a, 4a, 6a, and 8a), followed by a rate-limiting addition of water across the carbonyl oxide 1,3-dipole (reactions 3b, 4b, 6b, and 8b). We thus calculated bimolecular hydration rate constants with eq 9 (discussed in the Computational Methods section),<sup>93,94</sup> using the unimolecular rate constants in Table 7 and the equilibrium constants in Table 8. Our results are presented in Table 9. Our predictions for the reactions

**TABLE 9: CVT Rate Constants (cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) for CI Hydration Reactions**

	200 K	250 K	298 K
reaction 3	$1.04 \times 10^{-23}$	$5.43 \times 10^{-22}$	$7.23 \times 10^{-21}$ ( $4.23 \times 10^{-20}$ ) <sup>a</sup> ( $1.17 \times 10^{-20}$ ) <sup>b</sup>
reaction 4	$4.87 \times 10^{-17}$	$1.38 \times 10^{-16}$	$2.87 \times 10^{-16}$ ( $2.54 \times 10^{-15}$ ) <sup>a</sup> ( $6.72 \times 10^{-16}$ ) <sup>b</sup> ( $\sim 2 \times 10^{-16}$ ) <sup>c</sup>
reaction 6	$2.36 \times 10^{-22}$	$4.35 \times 10^{-21}$	$3.43 \times 10^{-20}$
reaction 8	$4.12 \times 10^{-24}$	$1.24 \times 10^{-22}$	$1.62 \times 10^{-21}$

<sup>a</sup> From Anglada et al.<sup>27</sup> <sup>b</sup> From Ryzhkov and Ariya.<sup>29</sup> <sup>c</sup> From Paulson and co-workers.<sup>26</sup>

of *syn* and *anti* acetaldehyde oxide agree with the predictions of Anglada et al.<sup>27</sup> and with those of Ryzhkov and Ariya<sup>29</sup> to within an order of magnitude. The rate constant we have predicted for reaction 4 matches the estimate ( $\sim 2 \times 10^{-16}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>) made by Paulson and co-workers<sup>26</sup> based on their measurement of the rate of the CH<sub>3</sub>CHOO + CH<sub>3</sub>CHO reaction and previous relative rate data. (Paulson's estimate did not differentiate between the *syn* and *anti* conformers, but since the *anti* form reacts with H<sub>2</sub>O 4 orders of magnitude faster than the *syn* form, the direct comparison we are making is appropriate.)

**D. Atmospheric Implications and Further Comparisons to Experiment.** Table 10 directly compares the tunneling-corrected rate constants for unimolecular isomerization and hydration for each of the four CIs under consideration. The hydration predictions are reported as pseudo first-order rate constants based on the saturation number density of water vapor at a given temperature (assuming perfect gas behavior).<sup>118</sup> At the temperatures found in the troposphere, all thermalized CIs with *syn*-methyl groups are predicted to undergo 1,4-hydrogen shifts from 3 to 8 orders of magnitude faster than the CIs' reactions with water. We therefore predict that water monomer is incapable of intercepting these three thermalized CIs. Assuming that the product of the 1,4-hydrogen shift, the vinyl hydroperoxide, decomposes with unit efficiency to give •OH, RH should therefore have no impact on •OH yield in the ozonolysis of *trans*-2-butene and isoprene. Our results also suggest that on the time scales characteristic of smog chamber experiments, the •OH yield from *trans*-2-butene and isoprene ozonolysis will not vary with pressure, since both chemically activated and thermalized *syn* CI will afford •OH. This is

**TABLE 10: First-Order and Pseudo-First-Order Tunneling-Corrected Rate Constants (s<sup>-1</sup>) for CI Reactions Based on the Saturation Number Density (molecules cm<sup>-3</sup>) of Water Vapor**

	200 K	250 K	298 K
species <b>1</b>			
reaction 1	$9.70 \times 10^{-2}$	$1.48 \times 10^0$	$2.42 \times 10^1$
reaction 3	$6.22 \times 10^{-10}$	$1.19 \times 10^{-5}$	$5.57 \times 10^{-3}$
species <b>1<math>\alpha</math></b>			
reaction 5	$9.17 \times 10^{-1}$	$1.12 \times 10^1$	$1.46 \times 10^2$
reaction 6	$1.41 \times 10^{-8}$	$9.56 \times 10^{-5}$	$2.64 \times 10^{-2}$
species <b>1<math>\beta</math></b>			
reaction 7	$4.97 \times 10^{-2}$	$8.27 \times 10^{-1}$	$1.47 \times 10^1$
reaction 8	$2.47 \times 10^{-10}$	$2.73 \times 10^{-6}$	$1.25 \times 10^{-3}$
species <b>4</b>			
reaction 2	$2.03 \times 10^{-4}$	$4.51 \times 10^{-1}$	$6.72 \times 10^1$
reaction 4	$2.92 \times 10^{-3}$	$3.03 \times 10^0$	$2.21 \times 10^2$
saturation [H <sub>2</sub> O] <sup>118</sup>	$5.99 \times 10^{13}$	$2.20 \times 10^{16}$	$7.70 \times 10^{17}$

consistent with the experimental findings of Fenske et al. for *trans*-2-butene ozonolysis.<sup>35</sup>

One complication in the above comparison is that we have neglected the reaction of water dimer with *syn*-methyl CI (e.g., reaction 3' above). Ryzhkov and Ariya<sup>29</sup> have predicted that at 303 K and 100% RH, (H<sub>2</sub>O)<sub>2</sub> reacts with the parent CI, CH<sub>2</sub>OO, almost 3 orders of magnitude faster than H<sub>2</sub>O. A similar acceleration in the hydration of *syn*-methyl CI would make this process comparable in rate to the 1,4-hydrogen shift. However, more accurate electronic structure data are necessary to test this possibility.

The comparisons in Table 10 are based on high-pressure rate constants. Table 11S (in the Supporting Information) presents UNIMOL predictions of how the rate constants for the 1,4-hydrogen shift reactions vary with pressure. At standard temperature and pressure (298 K and 760 Torr), the isomerization rate constants for the three *syn*-methyl CIs are at 90–100% of their high-pressure limit values. At 10 Torr, the lowest pressure typically observed in the troposphere, the isomerization rate constants for these CIs are no lower than ~20% of the high-pressure limit. The thermal rate constants for the 1,4-hydrogen shift in the troposphere will therefore be at most 1 order of magnitude lower than those reported in Table 10. The ad hoc adjustments we made to the reaction barriers to account for variational and tunneling effects are admittedly crude, and the values in Table 11S should therefore be viewed as highly approximate. At the same time, we have not modeled falloff behavior for the hydration reactions (3,6, and 8); their rate constants under atmospheric conditions could be significantly smaller than the high-pressure limit values.<sup>119,120</sup> In conclusion, we predict that isomerization, and therefore •OH production, should be unimpeded by hydration in these systems.

The fate of the thermalized *anti* conformer of acetaldehyde oxide is less clear-cut. Table 10 reveals that in the range of temperatures present in the troposphere, the rates of dioxirane formation (reaction 2) and hydration (reaction 4) are within a factor of 10 of each other. Given the uncertainties in the barrier heights, we cannot predict precisely the branching ratio for these two pathways. However, it is reasonable to conclude from our predictions that for the *anti* conformer the bimolecular reaction (at 100% RH) is at least comparable to the unimolecular reaction in rate. This conclusion is consistent with the substantial evidence in the literature<sup>121</sup> that alkene ozonolysis leads to the formation of stabilized CI (SCI) that undergoes reaction with scavengers such as H<sub>2</sub>O, SO<sub>2</sub>, NO<sub>2</sub>, and aldehydes. Moreover, our results suggest that experiments which have probed SCI yields using the water reaction<sup>38,122</sup> have preferentially scavenged the *anti* CI conformer, as Johnson and Marston<sup>25</sup> have recently argued.

The RRKM/master equation simulations allow us to make three quantitative comparisons with experiment. First, the variational transition state theory results summarized in Table 10 confirm that •OH yields measured in scavenger and tracer experiments arise from the 1,4-hydrogen shift in both chemically activated and thermalized *syn* acetaldehyde oxide **1**. The total yield of **1** from *trans*-2-butene ozonolysis is 0.661 (Figure 3). At 1 atm, the yield of vinyl hydroperoxide **3** formed promptly from **1** is 0.293 (Table 4), and the yield of thermalized **1** is 0.692 (Table 4). The total •OH yield is therefore (0.661)(0.293 + 0.692) = 0.651. (Note that this is very close, but not equal, to the total yield of **1**, since a small fraction of chemically activated **1** isomerizes to the dioxirane.) Our prediction is consistent with the experimental consensus<sup>5,28,32,34–37</sup> that the •OH yield lies between 0.52 and 0.67.

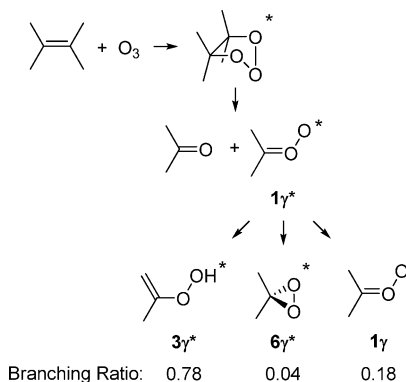
Other mechanistic pathways may contribute to the total •OH yield from *trans*-2-butene ozonolysis. Inspired by the early LIF measurements of Gutman and Nelson<sup>123</sup> and Lorenz et al.,<sup>124</sup> our laboratory reported computational evidence<sup>20,115</sup> that some fraction of the vinoxy radical cogenerated with •OH when the vinyl hydroperoxide decomposes (see Scheme 2 above) can react with O<sub>2</sub>, isomerize, and decompose to afford a second equivalent of •OH. Our rudimentary RRKM/master equation simulations indicated that •OH production from the vinoxy-O<sub>2</sub> adduct decreased markedly as bath gas pressure increased from 1 Torr to 1 atm. Subsequently, a far more rigorous computational study of the vinoxy + O<sub>2</sub> reaction by Delbos et al.,<sup>119</sup> along with preliminary experimental results from Oguchi reported therein, suggested that at 1 atm, the yield of •OH from vinoxy oxidation is close to zero. Kroll et al.'s<sup>22</sup> provocative LIF study of the ozonolysis of 3-hexenes with vinylic deuteriums provided evidence that up to one third of the hydroxyl radical generated may arise from decomposition of the carboxylic acid formed from *anti* CI (see Scheme 2 above). Their experiments, conducted at 6 Torr, did not probe the effect of varying bath gas pressure. However, it is reasonable to assume that •OH production from the acid, like that from the vinoxy-O<sub>2</sub> adduct, will decrease markedly as the pressure approaches 1 atm. Therefore, the isomerization and decomposition of *syn* CI is likely to account for most of the •OH observed at 1 atm.

Second, the total yield of *anti* acetaldehyde oxide **4** from *trans*-2-butene ozonolysis is 0.339 (Figure 3). At 1 atm, the fraction of **4** that either starts or ends up vibrationally cold is 0.620 (Table 5). As discussed above, this SCI can either isomerize to the dioxirane (reaction 2) or react with water to form the α-hydroxy hydroperoxide **10** (reaction 4). Based on Table 10, we can predict that at 100% RH and 298 K, the branching ratio for the water reaction is  $221 \text{ s}^{-1} / (221 \text{ s}^{-1} + 67.2 \text{ s}^{-1}) = 0.767$ . The total yield of **10** is therefore  $(0.339)(0.620)(0.767) = 0.161$ . This lies just outside the experimental confidence interval,  $0.24 \pm 0.07$ , reported by Paulson and co-workers<sup>38</sup> for the SCI yield from *trans*-2-butene ozonolysis based on the combined yield of **10** and its main decomposition product, H<sub>2</sub>O<sub>2</sub>, in the limit of high RH. (At high RH, the total yield of **10** + H<sub>2</sub>O<sub>2</sub> was 0.32; there was a background yield of **10** + H<sub>2</sub>O<sub>2</sub> of 0.08 attributed to peroxy radical reactions, not to reactions with SCI.) The reaction of **4** with water dimer (reaction 4' above), as reported by Ryzhkov and Ariya<sup>29</sup> but neglected in our study, will enhance the yield of **10** + H<sub>2</sub>O<sub>2</sub>.

Third, we can estimate the average unimolecular decomposition rate of thermalized acetaldehyde oxide at 298 K. Table 10 reports unimolecular rate constants of  $24.2 \text{ s}^{-1}$  for the thermalized *syn* conformer and  $67.2 \text{ s}^{-1}$  for the thermalized *anti* conformer. As noted above, the overall 1-atm yield of thermalized *syn* CI is  $(0.661)(0.692) = 0.457$ , and that of thermalized *anti* CI is  $(0.339)(0.620) = 0.210$ . The average unimolecular rate is therefore  $[(0.457)(24.2 \text{ s}^{-1}) + (0.210)(67.2 \text{ s}^{-1})] / (0.457 + 0.210) = 37.7 \text{ s}^{-1}$  at 298 K. This is a factor of 2 lower than the unimolecular rate of  $76 \text{ s}^{-1}$  reported by Paulson and co-workers<sup>26</sup> in their experimental study of acetaldehyde oxide formed in *trans*-2-butene ozonolysis. However, our prediction does fall within their confidence interval of  $[25 \text{ s}^{-1}, 230 \text{ s}^{-1}]$ .

**E. Mechanistic Implications for Other Alkenes.** Our calculations provide explicit evidence that all thermalized *syn* acetaldehyde oxide and *syn* methyl vinyl carbonyl oxide will form •OH, regardless of RH. To what extent can this be generalized to other alkenes whose ozonolysis generates *syn*-alkyl CI? One challenge to our simple model is posed by 2,3-



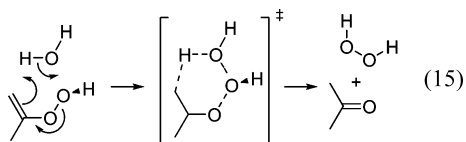
**SCHEME 4: Master Equation Results for 2,3-Dimethyl-2-butene Ozonolysis**


dimethyl-2-butene. A seminal RRKM/master equation study by Cremer and co-workers<sup>9</sup> predicted the branching ratios shown in Scheme 4 for a bath gas pressure of 1 atm and an  $\langle E_d \rangle$  value of 250 cm<sup>-1</sup>.

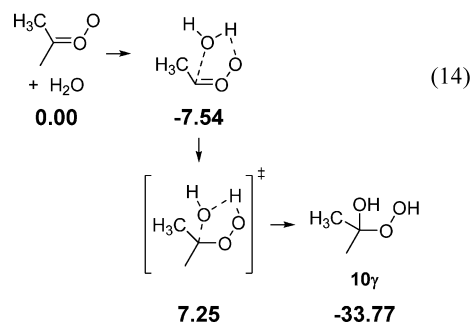
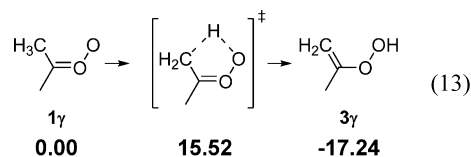
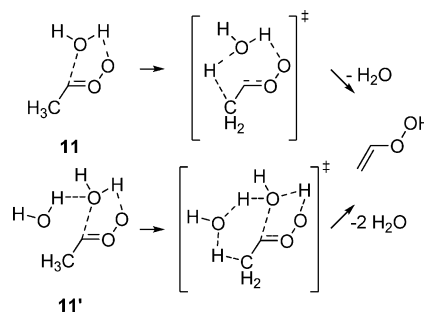
Cremer's master equation and specific adiabatic channel model calculations on hydroperoxide **3γ\*** predict ~100% decomposition to •OH and 1-methylvinoxy radicals; none of the **3γ\*** is collisionally stabilized at 1 atm. In preliminary work to predict the fate of the 18% of acetone oxide (**1γ**) that is thermalized, we have calculated MCG3//QCISD/6-31G(d) energies for the 1,4-hydrogen shift and hydration. Scheme 5 shows the zero-point corrected relative energies (in kcal mol<sup>-1</sup>) for these reactions.

Compared to the analogous reactions of *syn* acetaldehyde oxide (Tables 1 and 2), the barriers for both reactions 13 and 14 are 1–2 kcal mol<sup>-1</sup> lower in energy. Without performing the CVT and tunneling calculations, we can still make the qualitative prediction that reaction 13 should dominate. The yield of SCI, as inferred by formation of **10γ** and its derivatives, should therefore be zero, and, based on Cremer's simulation results in Scheme 4, the total •OH yield should be 0.96. In contrast, the Atkinson,<sup>125</sup> Marston,<sup>12</sup> and Paulson<sup>36</sup> groups report experimental •OH yields of 0.80–0.91, and Paulson and co-workers<sup>38</sup> report an SCI yield of 0.10. Thus, there is considerable experimental evidence that acetone oxide is not 100% efficient at generating •OH.

One way to explain this surprising result is Johnson and Marston's proposal,<sup>25</sup> based on some preliminary FTIR spectral data, that some of the vinyl hydroperoxide **3γ** formed in the *thermally* activated 1,4-hydrogen shift (reaction 13) is collisionally stabilized before it has a chance to decompose. This is consistent with the pressure dependence observed by Kroll et al.<sup>10</sup> in their study of 2,3-dimethyl-2-butene ozonolysis: the steady-state •OH yield was ~1.0 at 10 Torr, but was only ~0.8 at 100 Torr. Why would collisional stabilization of **3γ** lower the •OH yield? To explain the reduction in •OH, as well as account for Paulson's 10% yield of SCI, we propose a new reaction of vinyl hydroperoxide with water (reaction 15) that would interfere with the formation of hydroxyl free radicals:



Reaction 15 is consistent with Paulson's SCI scavenging study in that no hydroperoxide **10γ** was directly observed; rather, its

**SCHEME 5: MCG3 Energetics for Acetone Oxide Reactions**

**SCHEME 6: Alternative Hydration Pathways for *Anti* Acetaldehyde Oxide**


production was inferred by the observed increase in H<sub>2</sub>O<sub>2</sub> yield when RH was varied from 0% to 78%.

The other major challenge to our model of •OH production from *syn*-alkyl CI comes from the surprising smog chamber study of Wegener et al.,<sup>32</sup> who report that •OH yield *increases* with RH in the ozonolysis of propene, 1-butene, isobutene, and *cis*-2-butene, and the very recent work by Tillmann et al.<sup>106</sup> reporting the same phenomenon for α-pinene ozonolysis. All existing ozonolysis mechanisms predict either that •OH yield is unaffected by RH (as argued for here), or that •OH yield decreases with increasing RH because the hydration of CI leads to a hydroperoxide with a stable peroxy bond.<sup>28</sup> As mentioned earlier, Anglada and co-workers<sup>27,105</sup> have presented computational evidence for reactions like 3c in which hydration of the *syn*-alkyl CI would form a vinyl hydroperoxide with an unstable peroxy bond. Such reactions, however, would leave the •OH yield unaffected by RH, not cause it to increase. One way that RH could enhance •OH yield is if reactions analogous to reaction 3c occurred for *anti* CI, as shown in Scheme 6.

The direct transfer of an allylic hydrogen to the oxygen atom in water several Å away, as depicted for the reaction of **11**, is rather implausible. However, as Ryzhkov and Ariya have established,<sup>29,126</sup> reactions of water dimer with CI (as in **11'**) play important roles in atmospheric chemistry. Certainly, the transfer of a hydrogen atom from the methyl group to the peroxy group via a water dimer would be geometrically more plausible.

**IV. Conclusions**

Our multipronged computational study provides direct evidence for two ideas already considered in the experimental and



computational studies by Kroll and Donahue,<sup>10,112</sup> Johnson and Marston,<sup>25,30</sup> Hasson and Paulson,<sup>28,38,122</sup> Zhang,<sup>40,41</sup> and Atkinson<sup>31</sup> in the past decade: (1) The production of •OH from *syn*-alkyl CI happens on two time scales but is unaffected by RH. (2) SCI yields reflect only the amount of *anti* CI that is either formed vibrationally cold or rendered so by collisions with bath gas. Deviations from these generalizations may reflect the existence of hitherto unconsidered reactions of water with vinyl hydroperoxide and *anti* CI (as in reaction 15 and Scheme 6), and we are currently exploring these reactions in our laboratory. We are also treating reactions 3' and 4' with the high-level MCG3//QCISD/6-31G(d) model chemistry to determine the importance of the water dimer reactions emphasized by Ryzhkov and Ariya.<sup>29</sup> The paradigm that *syn* and *anti* CIs have distinct reactivities, clearly articulated by Cremer<sup>13,127</sup> and Anglada<sup>14</sup> some 15 years ago, applies not only to unimolecular reactions, but also to bimolecular reactions with water. Our laboratory is currently dissecting the origin of this conformational effect, and seeing if this *syn/anti* distinction holds for other SCI scavengers like SO<sub>2</sub> and NO<sub>2</sub>.

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**Supporting Information Available:** Coordinates of all of the stationary points considered in this article and the results of the UNIMOL simulations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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