Reaction of Criegee Intermediates with Water Vapor—An Additional Source of OH Radicals in Alkene Ozonolysis?

Alam S. Hasson,*[†,‡] Myeong Y. Chung,[‡] Keith T. Kuwata,[§] Amber D. Converse,[§] Debra Krohn,[†] and Suzanne E. Paulson[‡]

Department of Chemistry, California State University Fresno, Fresno, California, Department of Atmospheric Sciences, University of California at Los Angeles, Los Angeles, California, and Department of Chemistry, Macalester College, St. Paul, Minnesota

Received: March 8, 2003; In Final Form: June 18, 2003

The yields of OH radicals from the ozonolysis of ethene and *trans*-2-butene under dry and humid conditions (0% and 65% relative humidity, respectively) were measured by the small-ratio relative rate technique. The OH yields from both alkenes are found to be independent of the humidity within the error limits of the experiments. This suggests that the OH yield from the reaction of Criegee intermediates with water is less than 30%. These findings are supported by Master equation calculations that are consistent with the major product from the reaction of Criegee intermediates with water being the hydroxyalkyl hydroperoxide (RCH(OH)OOH), with a smaller contribution from OH. Implications of these results for both the fundamental reaction mechanism of ozone-alkene reactions and the fate of Criegee intermediates in the troposphere are discussed.

Introduction

Unsaturated hydrocarbons are significant primary pollutants in the boundary layer, comprising about 12% of the total of volatile organic compounds (VOCs) in urban air.[1] Alkenes typically have relatively short atmospheric lifetimes (minutes−hours) because of their reactivity toward OH radicals and ozone.[2] As a result of their unique chemistry, ozone−alkene reactions are potentially a major source of HO_x radicals (defined as OH + HO_2), for example,[3] hydroperoxides[4−7] and carboxylic acids[2] in the troposphere. To evaluate the importance of these reactions in the atmosphere, the mechanism of the formation of these products must be understood. Despite significant advances made in recent years, however, a complete understanding of gas-phase alkene ozonolysis has remained elusive.

It is now well established that ozone-alkene reactions can generate large quantities of OH radicals. OH yields have been measured for a range of alkenes by chemical tracer methods, for example,[8] by laser-induced fluorescence (LIF)[9−11] and by electron-spin resonance (ESR)[12]. Yields are found to be in the range 10−100%; see, for example, ref 2. In the initial stages of the ozone−alkene reaction, ozone adds across the double bond (R1) to form a primary ozonide, which then undergoes a rapid cycloreversion reaction[13,14] (R2) to form a carbonyl compound, and a carbonyl oxide (or Criegee intermediate).[15]

Asymmetric carbonyl oxides may be generated in either the syn- or anti- conformation.[15,16] The two forms are chemically distinct because the activation energy for the interconversion of these species is large.[17] It is generally accepted that most OH radicals are formed from the *syn*-carbonyl oxide via isomerization to a vinyl hydroperoxide (R3) followed by cleavage of the O−OH bond (R4).[18−20] The ozone−alkene reaction is extremely exothermic, and about 60 kcal/mol is released into the products of reaction R2. Because the activation energy for reaction R3 is only about 15 kcal/mol (see, for example, ref 20), a significant fraction of the carbonyl oxides may be formed with enough internal energy to react, and the excited carbonyl oxide may rapidly rearrange and decompose to form OH. Alternatively, the excited carbonyl oxide may lose energy via collisions with bath gas molecules and become energetically stabilized (R_d). The stabilized carbonyl oxide may also form OH via reactions R_a, R3, and R4, but on a much slower time scale.[10]

Experimental OH yields are largely consistent with an additional source of OH in these reactions. Very recently, a study of OH formation from isotopically labeled alkenes suggested that hydroxyl radicals may be formed from *anti*-carbonyl oxide via isomerization of the molecule to a carboxylic acid (R5) followed by cleavage of the C−OH bond (R6).[21] These experimental results may also be partially explained by the reaction of O_2 with the vinyl alkoxy radical formed in R4.[22] Although the origin of this additional OH has not yet been established, literature values of OH yields are consistent with up to 20% OH formation from these additional sources.[8,23]

The fraction of carbonyl oxide molecules that are stabilized by collisions (stabilized Criegee intermediate yield, Y_{SCI}) is somewhat unclear. A time-dependent LIF study of OH formation concluded that essentially 100% of the carbonyl oxides are stabilized at atmospheric pressure,[10,24] but several chemical tracer studies have shown that the stabilized Criegee intermediate yield is only 10−50%, see, for example, refs 6, 7, 23, 25, and 26, depending on the alkene. Resolution of this point is important because carbonyl oxides are known to react with a variety of different compounds, collectively known as Criegee scavengers (R7) and which include SO_2, carbonyl compounds, alcohols, carboxylic acids, and water.[2,25−27] In the presence of Criegee scavengers, OH formation from stabilized carbonyl

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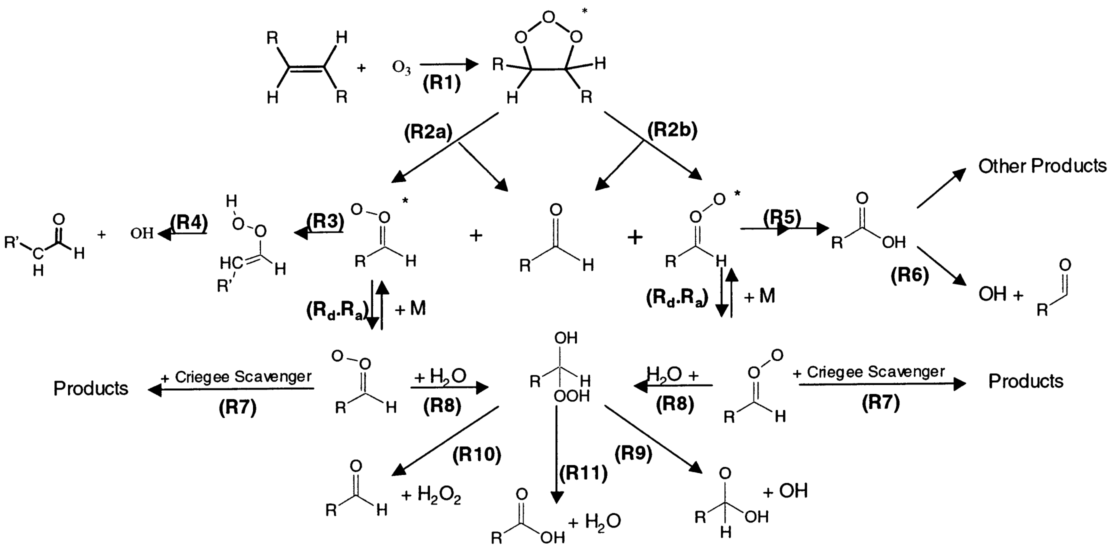
* To whom correspondence should be addressed. E-mail: ahasson@csufresno.edu.

[†] California State University Fresno.

[‡] University of California at Los Angeles.

[§] Macalester College.

10.1021/jp0346007 CCC: $25.00



oxide molecules is competitive with reaction R7. Thus, if OH is formed primarily from stabilized carbonyl oxides, the OH yield would be expected to change in the presence of Criegee scavengers except in the unlikely case that the OH yield from these reactions is the same as the OH yield from the unimolecular decomposition of the stabilized carbonyl oxide. OH formation from excited carbonyl oxides would be unaffected by the presence of Criegee scavengers because this reaction is much faster than reaction R7. Measurement of OH yields in the presence and absence of Criegee scavengers thus provides information regarding the source of OH (excited versus stabilized carbonyl oxide) in the ozone−alkene reaction.

In a recent study, Marston and co-workers found OH yields from 2-methyl-2-butene ozonolysis to be unaffected by the presence of a variety of Criegee scavengers.[28] The authors concluded that the reaction of carbonyl oxide with Criegee scavengers (R7) was too slow to compete with the decomposition of the stabilized Criegee intermediate (R_a + R3 + R4). This apparently contradicts the results of their previous study,[23] in which they measured yields of the products from reactions (R7) for the same alkene. The earlier study implies that a significant fraction of the stabilized carbonyl oxides survive long enough to react with Criegee scavengers. An explanation that is consistent with their previous work is that OH is formed only from excited carbonyl oxides, and not from stabilized carbonyl oxides.

Anglada and co-workers have carried out quantum calculations on the carbonyl oxide reaction with H_2O for the molecules CH_2OO, *syn*- and *anti*-CH_3CHOO, and $(CH_3)_2COO$.[29,30] For all four Criegee intermediates, they find that the lowest energy pathway is the formation of the hydroxyalkyl hydroperoxide, hereafter referred to as the HAHP (R8). This hydroperoxide is formed with enough internal energy to decompose via cleavage of the peroxy bond to form OH (R9). The coproduct of this reaction is a hydroxyalkoxy radical that would subsequently react with oxygen to form a carboxylic acid and HO_2; see, for example, ref 31. Additionally, the hydroperoxide may decompose to form a carbonyl and hydrogen peroxide (R10) or a carboxylic acid and water (R11). The latter pathways (R10 and R11) have higher activation energies than OH formation (R9); hence, the authors speculate that this pathway may lead to an increase in the OH yield when alkene ozonolysis is carried out in the presence of water vapor. Atkinson and co-workers[32,33] measured OH yields from various alkenes as a function of relative humidity using cyclohexane as an OH-radical scavenger and found no dependence on the water concentration. This technique is known to result in rather large uncertainties in OH yields, which could potentially mask a systematic variation in OH yield as a function of RH. Very recently, the same group[34] measured OH yields from a series of terpenes at RH in the range 5−50% using a more accurate technique. The authors again reported that the OH yields are independent of the humidity within the uncertainties of the experiments. These results may be explained either by rapid stabilization of the relatively large HAHP formed in reaction R8 or by differences in the activation energies for R9−11 compared to the barriers for the smaller HAHPs studied by Anglada and co-workers.

In this study, OH yields have been measured for the reactions of ozone with ethene and *trans*-2-butene at 0% and 65% relative humidity (RH). Additionally, master equation calculations have been performed for the reactions of the appropriate carbonyl oxide with H_2O to aid in the interpretation of the experimental results. OH yields in these experiments depend on the yields of excited and stabilized Criegee intermediates, the relative rates of the unimolecular decomposition of the stabilized Criegee intermediates versus their bimolecular reaction with water, and the branching ratio of the OH-forming channel in the unimolecular decomposition of the hydroxyalkyl hydroperoxide. The data thus provide information on the mechanism of OH formation in gas-phase alkene ozonolysis.

Experimental and Computational Section

OH yields were measured using the small-ratio relative rate technique (SRRRT) as described in detail previously.[35] The apparatus used has been employed in both OH yield studies, ref 36, and RH-dependent product yield studies of ozone-alkene reactions, ref 6. In brief, 5−10 ppm of the alkene and 0.2−0.45 ppm of pairs of chemical tracers (1,3,5-trimethylbenzene, *meta*-xylene, and di-*n*-butyl ether) were introduced into a 240 L Teflon reaction chamber in a stream of air humidified with a water bubbler. After equilibration, aliquots of ozone were introduced into the reaction chamber by passing pure O_2 over a low-pressure mercury lamp. Hydrocarbon concentrations were monitored by gas chromatography with flame ionization detection (GC-FID), and the OH yields were determined by comparison of the alkene and chemical tracer concentrations to the output from a detailed chemical model.

Master equation calculations were carried out using the MULTIWELL suite of programs.[37,38] Molecular geometries

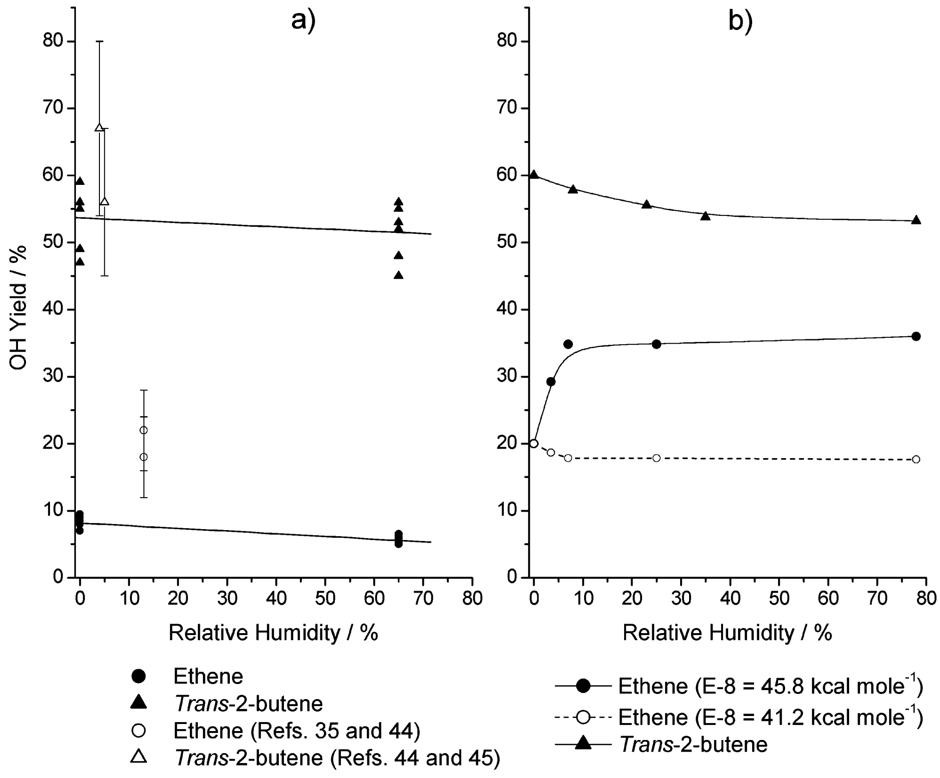


Figure 1. OH yields from ozone-alkene reactions as a function of relative humidity from (a) experiment and (b) master equation calculations using eqs E2 and E2b (see text for details).

and vibrational frequencies were calculated at the B3LYP/6-31G(d,p) level[39] using Gaussian 98.[40] Two sets of calculations were used to obtain values for the activation energies of the key reactions. First, electronic energies of molecules were taken from CCSD(T)/6-311+G(2d,2p)[41] calculations carried out by Anglada and co-workers.[29,30] Second, CBS-QB3[42] calculations were performed. This composite method approximates a CCSD-(T) calculation with a very large basis set. The CBS-QB3 energetics were based on geometries optimized with the larger 6-311G(2d,d,p) basis set. The exponential-down model for vibrational energy transfer was used, with the average energy transferred per collision, $\langle E_d \rangle$, assumed to be 300 cm^{-1}. This parameter was varied between 100 and 1000 cm^{-1} to investigate the effects of this assumption.

Quantum calculations indicate that the decomposition of the hydroxyalkyl hydroperoxide to form OH (R9) proceeds through a loose transition state; hence, microcanonical variational transition state theory using the minimum sum of states criterion was used to calculate rate coefficients for these reactions.[43] In brief, an estimate of the upper limit for the microcanonical rate coefficient was obtained by finding the minimum sum of states for the molecule as the RCH(OH)O−OH distance (r) was varied. Frequencies of vibrations in the parent hydroperoxide that are correlated with vibrations in the separated fragments were assumed to have the form

$$\nu(r) = \nu(r_e)\exp(-\alpha(r - r_e)) + \nu_\infty\{1 - \exp[-\alpha(r - r_e)]\} \qquad \text{(E1)}$$

where $\nu(r)$ is the vibrational frequency at distance r, $\nu(r_e)$ is the vibrational frequency in the parent molecule, ν_∞ is the vibrational frequency in the separated fragments, and α is an adjustable parameter, which was set to 1 Å^{-1}. Transitional frequencies in the parent hydroperoxide were assumed to have the same functional form, but with ν_∞ set equal to zero. A Morse potential with a Morse parameter of 1.9 Å was assumed for the electronic potential energy. The sensitivity of the Master equation calculations to the assumed Morse parameter and α was investigated by varying these values by ±30% and ±50%, respectively.

TABLE 1: Summary of Experimental Results

alkene	relative humidity/%	Y_{OH}
ethene	0	0.08 ± 0.01
	65	0.06 ± 0.01
trans-2-butene	0	0.54 ± 0.05
	65	0.52 ± 0.04

Results and Discussion

OH−Yield Experiments. Measured OH yields for ethene and *trans*-2-butene ozonolysis under dry and humid conditions are summarized in Table 1 and are shown in Figure 1a. Included for comparison are results from previous OH-yield studies from this laboratory, which were measured at 13% RH.[44,45] Yields measured here are systematically lower than those determined previously. In the case of *trans*-2-butene, current and previous OH-yield measurements (54% and 59%, respectively) lie within the mutual uncertainties. The OH-yields measured for ethene, however, are significantly different to those measured in an earlier study in this laboratory. The reason for this discrepancy is unclear, but does not affect the principal experimental findings of this study regarding trends in OH yields as a function of relative humidity.

As the humidity was increased from 0 to 65%, the OH yield for ethene was found to fall from 8% to 6%. This slight decrease in the OH yield is statistically insignificant given the uncertainties in the data. Likewise, for *trans*-2-butene, a small drop in the OH yield was observed as the humidity increased (from 54% at 0% RH to 52% at 65% RH). Once again, this decrease is smaller than the uncertainties in the measured OH yields.

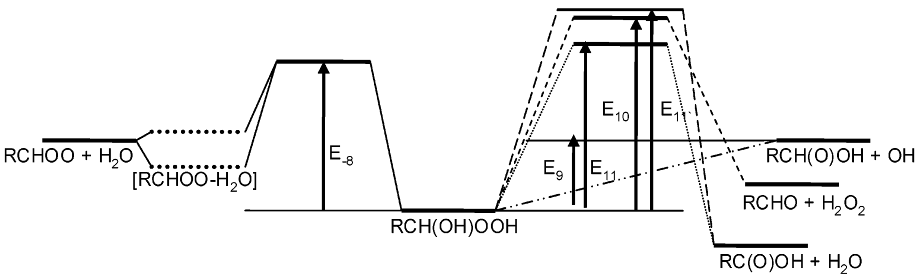


Figure 2. Activation energies for the unimolecular decomposition of HAHP (RCH(OH)OOH) (E11 and E11′ represent two distinct pathways for reaction R11).

TABLE 2: Activation Energies for the Unimolecular Decomposition of HAHP (RCH(OH)OOH)

		activation energy/kcal mol^{-1}	
hydroperoxide	reaction	CCSD(T) [30,29]	CBS-QB3
$CH_2(OH)OOH$	R-8	44.9	45.8
	R9	38.2	43.8
	R10	48.6	48.5
	R11	44.9	45.9
	R11′	48.2	49.3
$CH_3CH(OH)OOH$	R-8	38.2 (*anti*-CH_3CHOO)	41.8 (*anti*-CH_3CHOO)
		42.7 (*syn*-CH_3CHOO)	43.8 (*syn*-CH_3CHOO)
	R9	38.6 (*anti*-CH_3CHOO)	45.0 (*anti*-CH_3CHOO)
		37.6 (*syn*-CH_3CHOO)	44.0 (*syn*-CH_3CHOO)
	R10	45.6 (*anti*-CH_3CHOO)	45.8 (*anti*-CH_3CHOO)
		44.6 (*syn*-CH_3CHOO)	44.8 (*syn*-CH_3CHOO)
	R11	45.0 (*anti*-CH_3CHOO)	46.6 (*anti*-CH_3CHOO)
		44.0 (*syn*-CH_3CHOO)	45.6 (*syn*-CH_3CHOO)
	R11′	47.1 (*anti*-CH_3CHOO)	48.7 (*anti*-CH_3CHOO)
		46.1 (*syn*-CH_3CHOO)	47.7 (*syn*-CH_3CHOO)

The insensitivity of the OH yield from ethene ozonolysis to relative humidity demonstrates that the OH yield from the reaction of CH_2OO with H_2O (R8 + R9) is small. In the absence of water vapor, OH must be formed exclusively from the unimolecular decomposition of CH_2OO^* (R5 + R6). Under humid conditions, OH may also be produced from the reaction of CH_2OO with H_2O (R8 + R9). The two pathways for OH formation under humid conditions are competitive because the excited and stabilized forms of the Criegee intermediate may be interconverted via intermolecular collisional energy transfer (R_d, R_a), although these forms are not in equilibrium. Assuming that these reactions are the only sources of OH in these reactions, the OH yield is given by the equation

$$Y_{OH} = F_{CI}Y_{OH-R8} + (1 - F_{CI})Y_{OH-R5} \qquad (E2)$$

where Y_{OH} is the total OH yield from the ozonolysis reaction, F_{CI} is the fraction of Criegee intermediates reacting with water, Y_{OH-R8} is the OH yield from the reaction of CH_2OO with H_2O, and Y_{OH-R5} is the OH yield under dry conditions (which is equal to the OH yield from the unimolecular decomposition of CH_2OO^*). The equation implicitly assumes that [H_2O] is effectively constant and, thus, that reaction R8 is pseudo first order. Given that at 1% RH, the water concentration is more than an order of magnitude greater than the maximum alkene concentration used, this is clearly a valid assumption. The value for Y_{OH-R5} is taken to be 0.2[44,45] even though this number is considerably higher than the value obtained in this work. At 0% RH, F_{CI} is zero, whereas at high RH, F_{CI} is equal to Y_{SCI}. Assuming that HAHP and the OH-forming pathway are the only channels of the reaction of CH_2OO with H_2O and that the yield of hydroxymethyl hydroperoxide (HMHP) from reaction R8 is about 40% at 65% RH,[6] Y_{SCI} can be taken to be 0.4 at high RH. Using this information, the following expression can be obtained using E2 for the change in OH yield between dry and humid conditions (ΔY_{OH})

$$\begin{aligned}\Delta Y_{OH} &= Y_{OH}(RH = 65\%) - Y_{OH}(RH = 0\%)\\ &= (0.4Y_{OH-R8} + (1 - 0.4)0.2) - (0Y_{OH-R8} + (1 - 0)0.2)\\ &= 0.4Y_{OH-R8} - 0.08 \qquad (E2a)\end{aligned}$$

A value for ΔY_{OH} of 0.05 should be clearly observable in these experiments; therefore, Y_{OH-R8} is less than about 30% for CH_2OO.

The fact that the OH yields from trans-2-butene ozonolysis are independent of the relative humidity shows that OH production from *syn*-carbonyl oxide occurs predominantly from internally excited Criegee intermediates and not stabilized Criegee intermediates. At 65% RH, about 25% of the Criegee intermediates react with water.[6] If these Criegee intermediates were *syn*-carbonyl oxide, then the OH yield would show a marked decrease as the relative humidity increases. Because this does not occur, the data support the assertion that the majority of stabilized Criegee intermediates are *anti*-carbonyl oxides. The preceding argument assumes that the OH pathway for the reaction of CH_3CHOO with H_2O (R8 + R9) is not a major product channel. This assumption is supported both by the experimental results for the ethene reaction outlined above and results from the master equation calculations (see below).

Calculations

Activation energies for the unimolecular decompositions of hydroxymethyl hydroperoxide (HMHP) and hydroxyethyl hydroperoxide (HEHP) are shown in Figure 2 and Table 2. Formation of the HAHP from the reaction of Criegee intermedi-

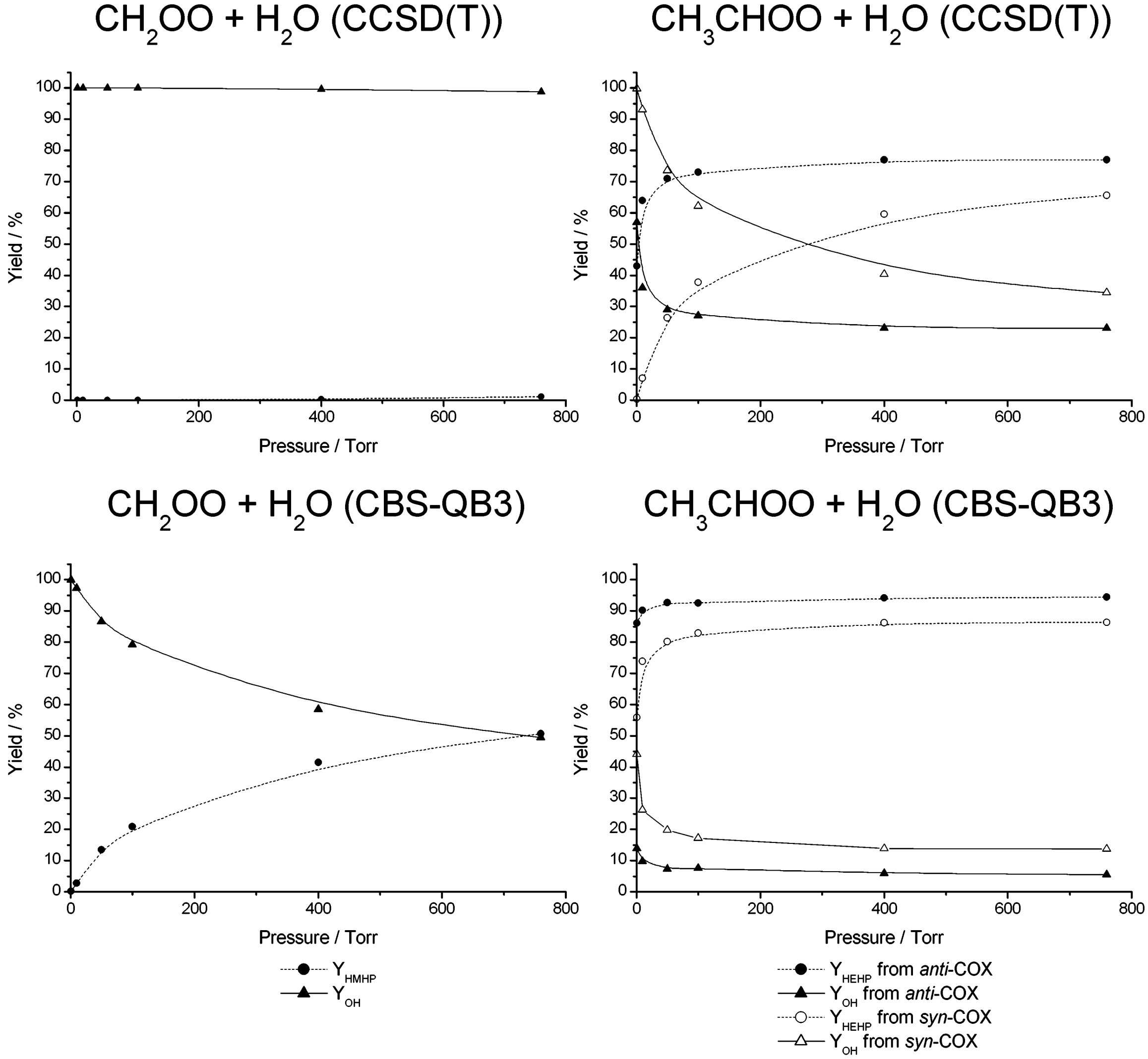


Figure 3. Calculated pressure-dependent product yields for the RCHOO + H_2O reaction.

ate with water (R8) is found to be exothermic by about 40 kcal/mol, and significant fractions of each chemically activated HAHP possess enough energy to decompose via reactions R9, R10, and R11. For both hydroperoxides, the smallest activation barrier leads to the formation of OH and a hydroxyl alkoxy radical via cleavage of the O−OH bond (R9). Because this reaction also proceeds through a loose transition state, it is reasonable to expect that reaction R9 dominates the chemistry of the hydroxyalkyl hydroperoxides (HAHPs). This intuitive picture is borne out by the Master equation calculations. Calculated pressure dependent product yields are shown in Figure 3. Under all conditions, the two principal products channels are the formation of energetically stabilized HAHP and OH (which is generated along with RCH(O)OH). Yields of H_2O_2 + RCHO and RC(O)OH + H_2O via reactions R10 and R11 are negligible. At low pressures, collisional deactivation of the chemically activated HAHP is slow; hence, OH radical formation dominates. As the pressure increases and approaches one atmosphere, intermolecular energy transfer is rapid, and stabilized HAHP becomes the major product.

Calculated product yields are sensitive to the degree of chemical activation, determined by the activation energy for reaction R-8 (E-8)

$$\mathrm{RCH(OH)OOH\ (+\ M)} \rightarrow \mathrm{RCHOO} + \mathrm{H_2O} \qquad \text{(R-8)}$$

and the activation energy of the OH-forming reaction channel (E9). CBS-QB3 calculations systematically yield a smaller ratio for E-8:E9 than the CCSD(T) calculations. Master equation calculations using the CBS-QB3 data thus predict HAHP yields that are higher than calculations using the CCSD(T) data at atmospheric pressure (Figure 3). In the case of *trans*-2-butene, the difference between the CCSD(T) and CBS-QB3 data is significant, but for both calculations, HEHP is the major product. For ethene, however, the difference between the two calculations is dramatic, with calculated HMHP yields of 0% and 50% for the CCSD(T) and CBS-QB3 data, respectively.

Master equation calculations were carried out to determine the sensitivity of the product yields to the assumed values for $\langle E_d \rangle$, α, and the Morse parameter. Calculations performed with $0.5 < \alpha < 1.5$ Å^{-1} and $1.3 <$ Morse parameter < 2.5 Å resulted in variations in product yields of less than 10% and 5%, respectively. Additional calculations were carried out with $\langle E_d \rangle = 100$ and 1000 cm^{-1}. Product yields were found to vary by less than 10% for the CBS-QB3 data, but by up to 40% for the CCSD(T) data. Hereafter, all calculated product yields refer to calculations performed with the CBS-QB3 data, and with $\alpha = 1$ Å^{-1}, Morse parameter = 1.9 Å, and $\langle E_d \rangle = 300$ cm^{-1} unless otherwise stated. At 760 Torr, calculated product yields for the reaction of CH_2OO with H_2O are 50% for HMHP and 50% for OH. Under the same conditions, the yields are 94%

and 6% for HEHP and OH, respectively, for the reaction of *anti*-CH_3CHOO with H_2O, and $Y_{HEHP} = 88\%$ and $Y_{OH} = 12\%$ for the *syn*-$CH_3CHOO + H_2O$ reaction.

Recently, yields of hydroperoxides in the ozonolysis of ethene and *trans*-2-butene were measured as a function of relative humidity.[6] These experimental yields (which correspond to F_{CI} in eq E2) can be combined with the calculated values for Y_{OH-R8} to predict OH yields as a function of relative humidity using equation E2 for ethene, and a related expression for *trans*-2-butene. The equation for *trans*-2-butene is more complicated than for ethene because two different Criegee intermediates with different values for F_{CI}, Y_{OH-R8}, and Y_{OH-R5} are formed in the ozonolysis reaction. The OH yield for this alkene is given by the expression

$$\begin{aligned} Y_{OH} = Y_s(F_{CI-s}Y_{OH-R8-s} + (1 - F_{CI-s})Y_{OH-R5-s}) + \\ Y_a(F_{CI-a}Y_{OH-R8-a} + (1 - F_{CI-a})Y_{OH-R5-a}) \quad \text{(E2b)} \end{aligned}$$

In this equation, Y_s and Y_a are the yields of *syn*-CH_3CHOO and *anti*-CH_3CHOO and are both assumed to be 50%. The remaining parameters are the same as those defined for eq E2, with s and a subscripts refereeing to *syn*- and *anti*-CH_3CHOO, respectively. F_{CI-s}, F_{CI-a}, $Y_{OH-R5-s}$, and $Y_{OH-R5-a}$ were estimated from refs 6 and 7, and $Y_{OH-R8-s}$ and $Y_{OH-R8-a}$ were taken from the Master equation calculations. The results of these calculations are shown in Figure 1. For ethene ozonolysis, the OH yield is expected to increase from 18% at 0% RH to 36% at 65% RH. This apparently contradicts the experimental data which show that the OH yield is independent of the water concentration. This discrepancy can, however, be accounted for by noting the sensitivity of the results to the barrier heights E-8 and E-9, as outlined above. Calculations in which the E-8 barrier height is reduced by 10% give results that closely match the experimental trend (Figure 1); thus, the experiments and calculations are consistent within their mutual uncertainties. The OH yield from *trans*-2-butene is predicted to decrease by 7% as the humidity increases from 0 to 65% RH. Calculations based in the CBS-QB3 activation energies agree with experiment better than those based on the CCSD(T) energies. The better agreement may, however, be fortuitous, as the master equation predictions are very sensitive to slight variations in activation energies. For both alkenes, the virtual independence of the OH yield from the relative humidity predicted by the calculations is in broad agreement with experimental results. Very recently, Orzechowska and Paulson[46] measured yields of carboxylic acids containing two or more carbon atoms from alkene ozonolysis under dry and humid conditions. They conclude from this work that acid formation from the reaction of Criegee intermediates with water (R8, R9, and R10) is a minor pathway. These results are consistent with the low OH yields from both the experimental measurements and calculations performed in this study.

In a recent study,[7] it was concluded that the formation of hydrogen peroxide and a carbonyl compound from the reaction of RCHOO with H_2O (R10) is significant for $>C_1$ Criegee intermediates, and is the dominant product channel for $>C_2$ Criegee intermediates. The calculations carried out here suggest that neither hydrogen peroxide nor carboxylic acids are formed directly from the chemically activated HAHP. In principle, these species may still be formed from the thermalized HAHP, either by unimolecular decomposition (R10a, R11a) or via bimolecular reactions with water molecules (R10b, R11b)

$$\mathrm{RCH(OH)OOH + M \rightarrow RCHO + H_2O_2 + M} \quad \text{(R10a)}$$

$$\mathrm{\rightarrow RC(O)OH + H_2O + M} \quad \text{(R11a)}$$

$$\mathrm{RCH(OH)OOH + H_2O \rightarrow RCHO + H_2O_2 + H_2O} \quad \text{(R10b)}$$

$$\mathrm{\rightarrow RC(O)OH + 2H_2O} \quad \text{(R11b)}$$

Quantum calculations indicate that the activation energies for these reactions are relatively large (>30 kcal/mol). These reactions are therefore extremely slow, and the thermalized HAHP molecules should have lifetimes of at least several years. It seems likely, therefore, that the high yields of hydrogen peroxide and carbonyl compounds formed in the humid ozone-alkene experiments are a result of heterogeneous decomposition of the HAHP during analysis.

Atmospheric Implications. Because the concentration of water vapor in the troposphere is often high, reaction with H_2O is likely to be an important sink for stabilized Criegee intermediates. The major product of this reaction is expected to be the HAHP. The reaction of Criegee intermediates with water (R8) should not have a significant impact on OH yields from alkene ozonolysis. In the atmosphere, the fate of the hydroxyalkyl hydroperoxide may be heterogeneous removal, reaction with OH, or photolysis. Photolysis may be a significant source of secondary OH radicals, because the O−OH bond is the most labile bond in the molecule. The coproduct of the photolysis of the HAHP would be a hydroxyalkoxy radical (RCH(OH)O), which would subsequently react with O_2 to form a carboxylic acid and HO_2; see, for example, ref 32. Additional work is required to establish removal rates of HAHPs from the atmosphere.

Acknowledgment. A.S.H. thanks the donors of the Petroleum Research Fund (American Chemical Society, #37996-GB6) and the College of Science and Mathematics, California State University at Fresno for financial support. K.T.K. and A.D.C. thank the donors of the Petroleum Research Fund (American Chemical Society, #38037-GB6) and the Violet Olson Beltmann Fund (Macalester College) for financial support and the National Computational Science Alliance facility at the University of Kentucky for computational resources.

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