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The Effect of Criegee-Intermediate Scavengers on the OH Yield from the Reaction of Ozone with 2-methylbut-2-ene

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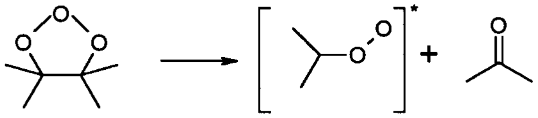
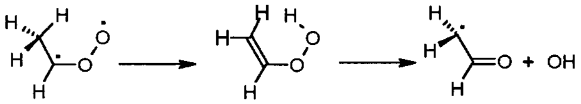
The yield of OH from the gas-phase reaction of ozone with 2-methylbut-2-ene has been measured in the presence of various molecules (H_2O, SO_2, butanone, and acetic acid) that can act as scavengers for the Criegee intermediates (CIs) formed in the reaction. No discernible difference is observed between experiments carried out in the presence and absence of these scavengers. The results indicate that the thermal decomposition of CIs that give OH radicals is fast compared with their bimolecular reaction with the scavengers under the conditions of the experiments. Combined with the results of a recent time-resolved study, upper limits (in units of cm^3 $molecule^{-1}$ s^{-1}) were determined for the bimolecular reactions of the CI with H_2O (1×10^{-16}), SO_2 (4×10^{-15}), butanone (2×10^{-14}), and acetic acid (1×10^{-14}). The results imply that these reactions are too slow to inhibit OH formation in the ozonolysis of alkenes and that the currently recommended OH yields can be used in models of atmospheric chemistry.

I. Introduction

The gas-phase reactions of ozone with alkenes have been the subject of considerable interest in recent years,[1] in large part because they are important processes in Earth's atmosphere.[2,3] Laboratory measurements have shown that OH radicals are generated in the reactions,[4−6] and yields of radical formation at atmospheric pressure have been measured using a range of different methods.[7−10] The exact nature of the mechanism of the reaction is not properly understood, but it has often been assumed that radical formation occurs via the decomposition of nascent vibrationally excited Criegee intermediates (CIs) formed following the decomposition of the primary ozonide.[1]



Theoretical calculations indicate that OH formation via the hydroperoxide channel proceeds with a relatively small barrier,[11]



and studies in this group have shown that measured OH yields are consistent with this mechanism.[9,12] However, new evidence has been provided by Kroll et al.,[13] who carried out a direct study of OH formation in the reactions of ozone with alkenes as a function of pressure. They showed that, as pressures approach one atmosphere, prompt formation is efficiently quenched in a few hundredths of a second. These observations clearly have implications for our understanding of the reaction mechanism because they imply that any OH formed in experiments at one atmosphere must result from the thermal decomposition of *stabilized* CIs on a relatively long time scale. The observations also have serious implications for our understanding of the importance of the reactions in atmospheric chemistry. CIs are believed to react with sulfur dioxide,[14] water,[15] organic acids,[16] carbonyl compounds,[17] etc.; if these reactions are sufficiently fast under atmospheric conditions, they could compete with the unimolecular channel, and OH would not be a significant product of ozone-alkene reactions. Given the potential importance of the reactions of ozone with alkenes as a source of OH in the atmosphere,[14] we have carried out some preliminary experiments to test whether the presence of CI scavengers has an effect on measured OH yield. The system chosen for study was the reaction of ozone with 2-methylbut-2-ene. This reaction has a high OH yield (0.82[9]) and also gives rise to the two CIs that are believed to generate OH by the hydroperoxide mechanism.

II. Methodology

As explained in more detail elsewhere,[9,18] yields of hydroxyl radicals can be determined by measuring the diminution in the concentration of a tracer compound, T, when in the presence of a reacting ozone−alkene system. The tracer concentration is given by

$$[\mathrm{T}] = [\mathrm{T}]_i - \frac{k_\mathrm{T}[\mathrm{T}]_i}{k_\mathrm{T}[\mathrm{T}]_i + k_\mathrm{A}[\mathrm{A}]_i + k_\mathrm{S}[\mathrm{S}]_i}\beta\Delta[\mathrm{O}_3]$$

where $[A]_i$ is the initial concentration of alkene; $[S]_i$ is the initial concentration of the CI scavenger; k_T, k_A, and k_S are the rate constants for the reaction of OH with T, A, and S; and β is the OH yield with respect to ozone consumed. A plot of [T] vs $\Delta[O_3]$ gives a slope of $-R$, where $R = k_T[T]\beta/(k_T[T] + k_A[A] + k_S[S])$. A plot of R vs $k_T[T]/(k_T[T] + k_A[A] + k_S[S])$ then yields β. For these experiments, 1,3-dimethylbenzene (DMB) was used as the tracer; this compound gave less scattered results than those obtained using 1,3,5-trimethylbenzene (TMB) in previous studies.[9, 18]

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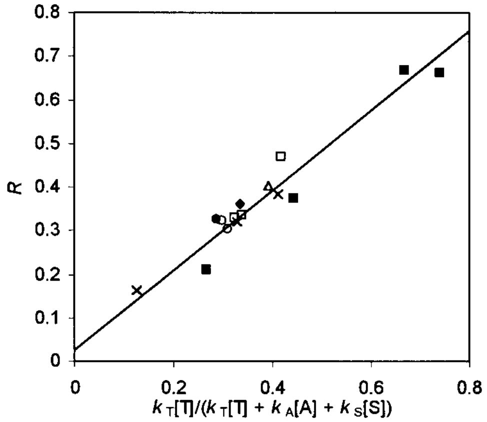

Figure 1. Plot of R vs $k_T[T]_i/(k_T[T]_i + k_A[A]_i + k_S[S]_i)$ for the ozonolysis of 2-methylbut-2-ene. □, DMB, no CI scavenger; ×, DMB, 20 000 ppmv H_2O; ○, DMB, 100 ppmv SO_2; ●, DMB, 500 ppmv SO_2; △, DMB, 100 ppmv butanone; ◆, DMB, 150 ppmv acetic acid; ■, TMB tracer experiments also included.

III. Experimental Section

The experimental apparatus employed for this study comprised a static reaction chamber with attached gas chromatograph (GC) with flame ionization detection (FID). A mixture of 2-methylbut-2-ene and the relevant OH tracer and/or CI scavenger (DMB, H_2O, SO_2, butanone, or acetic acid) was prepared in a 50 L collapsible Teflon chamber using dry synthetic air (BOC Gases, BTCA 74) as the diluent gas. Water vapor was introduced into the mixture by passing the synthetic air through three Dreschel bottles containing deionized water. Typical initial hydrocarbon concentrations employed were 10 ppmv of the alkene and 10−50 ppmv of DMB. Typical initial ozone mixing ratios ranged from ca. 0.5 to 8 ppmv. Experiments were carried out by admitting a known concentration of ozone, to a pressure of ca. 8 Torr, into a 0.5 L borosilicate glass reaction chamber and adding a sample of the hydrocarbon mixture such that a total pressure of 1 atm (760 ± 10 Torr) was effected. Experiments were carried out at 295 ± 2 K. Ozone was generated as a mixture in O_2 by passing oxygen through a Fischer ozone generator, its concentration being determined spectrophotometrically by absorption at $\lambda = 254$ nm. After the mixture was left for sufficient time for the ozone to react, the contents of the glass bulb were separated and detected by GC-FID (Perkin-Elmer, model 8420). This procedure was typically repeated for six different initial ozone concentrations during each study. Chromatographic peak heights were related to concentrations after calibration with pure standards. A 25 m × 0.53 mm diameter Poraplot Q capillary column was used. A typical temperature program employed held the column isothermally at 200 °C for 10 min. Sulfur dioxide was supplied by Aldrich (purity > 99.9%) and was used without further processing; all other reagents employed were of analytical grade and underwent a freeze−pump−thaw cycle before being used.

IV. Results and Discussion

Figure 1 shows a plot of R vs $k_T[T]/(k_T[T] + k_A[A] + k_S[S])$ for all experiments carried out in this study. Also included are the results of already-published experiments carried out using TMB as the tracer.[18] What the figure shows is that the measured OH yield is unaffected by the presence of H_2O, SO_2, butanone, and acetic acid, all of which are known to react with stabilized CIs. The concentration of the latter three species (≥100 ppm) was far in excess of their concentrations (or the concentrations of related compounds) in the atmosphere. It is clear, then, that the reactions of CIs with these types of species cannot inhibit OH formation in the reaction of ozone with 2-methylbut-2-ene under atmospheric conditions. At 295 K, the maximum concentration of H_2O used in our experiments (ca. 20 000 ppm) can be exceeded in the atmosphere by some 25%, but this small increase cannot have a significant effect on the OH yield. At higher temperatures, much higher concentrations are sometimes experienced, e.g., at 313 K, concentrations of water vapor of ca. 70 000 ppm are possible. However, the barrier to OH formation from syn CIs has been calculated[11] at approximately 60 kJ mol^{-1}. Consequently, the rate of formation of OH from the stabilized CI is expected to be about a factor of 4 faster at 313 K than it is at the temperature of the experiments described here. The rate constant for the bimolecular reaction between the CI and water may also be temperature dependent, but because this reaction is believed to be an addition reaction, the temperature dependence is likely to be weak; it is very difficult to envisage how the bimolecular reaction could have a stronger temperature dependence than the unimolecular decomposition. At temperatures below 295 K, unimolecular decomposition is less effective but concentrations of H_2O are necessarily lower, so that, competition from the bimolecular reaction can only be significant if the reaction has a strong negative temperature dependence. It therefore seems likely that, under atmospheric conditions, the formation of OH from the reaction of ozone with 2-methylbut-2-ene is not inhibited by the presence of water vapor.

TABLE 1: Upper Limits for the Reactions of CIs with a Number of Molecular Species

reactant	H_2O	SO_2	butanone	acetic acid
$[S]_{max}$/molecule cm^{-3}	5×10^{17}	1×10^{16}	2.5×10^{15}	4×10^{15}
k/cm^3 molecule^{-1} s^{-1}	$\leq 1 \times 10^{-16}$	$\leq 4 \times 10^{-15}$	$\leq 2 \times 10^{-14}$	$\leq 1 \times 10^{-14}$

It is important to know to what extent OH formation in the reactions of ozone with other alkenes is inhibited by the presence of CI scavengers. Although a small amount of OH is formed from the decomposition of the simplest CI, CH_2OO, most OH is formed via the decomposition of more complex types, such as *syn*-CH_3CHOO, $(CH_3)_2COO$, and structurally related analogues. The reaction of ozone with 2-methylbut-2-ene generates both types of CI, and so it is reasonable to suppose that the conclusions drawn about OH formation in this reaction can be extended to the reactions of ozone with other alkenes. This statement brings us to the major conclusion of this letter: the currently accepted OH yields for the reactions of ozone with alkenes are applicable to atmospheric conditions.

The measurements of Kroll et al. place limits on the lifetime of the stabilized CI. Limits can also therefore be placed on the rate constants for the bimolecular reactions of CIs with the molecular species used in our experiments. The Kroll et al. measurements were made at ca. 10 μs. If the lifetime for the formation of OH from the stabilized CI were shorter than this value, the OH yields would be expected to rise at higher pressures, the opposite of their observations. The only reaction for which the results indicate that this effect was observed is for the reaction of ozone with 2,3-dimethylbut-2-ene, but as the authors explain, at the higher pressures, the measurements were made at reaction times longer than 10 μs. The scatter in Figure 1 indicates that a reduction in OH yield of about 30% would be clearly detectable, and implies that $k_S[S] \leq 35$ s^{-1}. On this basis, upper limits for the bimolecular rate constants for the reactions of the CI with the scavenger molecules used in this study can be obtained and are listed in Table 1. Rate constants for the reactions of CIs with the molecules studied here have been quoted in the literature. However, the studies have used the relative-rate method, with an *assumed* value for the rate constant of the reference reaction.[1] It is therefore not possible to make meaningful comparisons between the upper limits for the rate constants listed in Table 1 and those in the literature. It should be noted that no attempt has been made to distinguish between the various types of CIs (*syn*-CH_3CHOO, *anti*-CH_3CHOO, and $(CH_3)_2COO$) formed in the reaction of ozone with 2-methylbut-2-ene. The results in Table 1 are obtained on the basis of the behavior of the CIs that decompose to give OH (i.e., CIs with an alkyl group syn to the terminal oxygen atom). However, there is no reason to assume that the reactivity of *syn*- and *anti*-CH_3CHOO toward molecular species should be significantly different. Rather, *anti*-CH_3CHOO is longer-lived than the syn conformer, and so has longer to react with other species, as has been observed.[14−17]

There has been some unpublished work from Anderson and co-workers[19] that shows, for tetramethylethylene, that at 10 and 100 Torr the yields of OH increase on the time scale of hundreds of milliseconds, as expected on the basis of their previous work.[13] In principle, this observation allows us to place more stringent limits on the values of the bimolecular rate constants in Table 1. However, Paulson and co-workers[20] have very recently reported a rate constant for the unimolecular decomposition of the CI from *trans*-2-butene of 76 s^{-1}, and we therefore prefer the upper limits in the table. In addition, this group also determined a bimolecular rate constant of 10^{-12} cm^3 $molecule^{-1}$ s^{-1} for the reaction of the CI with acetaldehyde.[20] This rate constant is significantly greater than any of the upper limits listed in Table 1.

V. Conclusions

The results presented in this letter show that the yield of OH in the reaction of ozone with 2-methylbut-2-ene is unaffected by the presence of large concentrations of species that are known to react with stabilized CIs. It is argued that this observation can be extended to other alkenes. On the basis of recently published work on the time-resolved detection of OH, upper limits for the bimolecular rate constants of CIs with several molecular species were presented. Most importantly of all, the study shows that the formation of OH from ozone−alkene reactions is important in the atmosphere, even though OH appears to be formed through the decomposition of the stabilized CI.

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