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# Rate Constants for Reactions of the Hydroxyl Radical with Several Partially Fluorinated Ethers

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**2. CSTR.** (a) *Pumps.* The pump system consisted of two identical Bishoff HPLC pumps. The flow rates could be adjusted over a range of  $10 \mu\text{L min}^{-1}$  to  $5 \text{ mL min}^{-1}$ .

(b) *Reactor.* The body of the reactor consisted of a quartz cylinder closed at both ends with Teflon blocks. The lower Teflon block contained the injectors, while the upper block was slightly conical to enable escape of bubbles. A micromagnetic stirrer was placed in the cylinder. The speed of stirring was controlled by a stepper motor. The setup was placed in a thermostated chamber inside a diode-array spectrophotometer (HP 8451). The internal volume of the reactor was 2.1 mL. The absorbance of the reacting solution was recorded through a 0.5 mm wide calibrated slit, giving an overall optical path length of 1.1 cm. Pure water was used as reference.

**3. Kinetics in Batch Reactor.** Measurements were made with the same solutions in the same reactor used as batch or CSTR. One pump fed in a solution of permanganate  $[\text{KMnO}_4] = 1.09 \times 10^{-3} \text{ M}$  and  $[\text{H}_2\text{SO}_4] = 0.54 \text{ M}$ . The other pump fed in a solution of oxalic acid (condition I,  $[\text{H}_2\text{C}_2\text{O}_4] = 1.82 \times 10^{-2} \text{ M}$ ; condition II,  $[\text{H}_2\text{C}_2\text{O}_4] = 2.73 \times 10^{-3} \text{ M}$ ). The solutions were pumped in at the maximum flow rate (5 mL/min for both pumps). The pumps were switched off and the UV/visible spectra recorded. The initial concentrations in the reactor were as follows:  $[\text{KMnO}_4]_0 = 5.45 \times 10^{-4} \text{ M}$ ;  $[\text{H}_2\text{SO}_4]_0 = 0.27 \text{ M}$ . I,  $[\text{H}_2\text{C}_2\text{O}_4]_0 = 9.10 \times 10^{-3} \text{ M}$ ; II,  $[\text{H}_2\text{C}_2\text{O}_4]_0 = 1.37 \times 10^{-3} \text{ M}$ .

**4. Determination of Steady States in the CSTR.** The two pumps operated at the same flow rate  $D$  (mL/min). The residence time  $\tau$  (s) is expressed by the relationship

$$\tau = 60 \times 2.1 / 2D$$

The absorbance at 560 nm was recorded until a steady state was reached. This took up to  $20\tau$ . To describe the zone of bistability,  $\tau$  was reduced from the thermodynamic to the flux branch;  $\tau$  was then increased from the flux to the thermodynamic branch. The two transitions from one branch to another were not observed at the same values of  $\tau$ .

**5. Data Treatment.** The experimental data (Abs versus  $t$ ) were transferred from the HP 8451 spectrophotometer to a HP 9000 Series 330 workstation running under UNIX. The software was written in C.

*Smoothing and derivation.* Both operations were carried out using the Savitsky-Golay's algorithm,<sup>23</sup> with a smoothing window width of 11 points and a third degree polynomial.

Registry No.  $\text{MnO}_4^-$ , 14333-13-2; oxalic acid, 144-62-7.

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## Rate Constants for the Reactions of the Hydroxyl Radical with Several Partially Fluorinated Ethers<sup>†</sup>

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We have measured rate constants for the reactions of the hydroxyl radical, OH, with a number of fluorinated ethers. These ethers and their calculated atmospheric lifetimes for removal by OH (in years), estimated relative to  $\text{CH}_3\text{CCl}_3$ , are as follows:  $\text{CF}_3\text{-O-CH}_3$ , 3.0;  $\text{CF}_3\text{-O-CHF}_2$ , 19;  $\text{CHF}_2\text{-O-CHF}_2$ , 2.6;  $\text{CF}_3\text{CH}_2\text{-O-CH}_3$ , 0.1;  $\text{CF}_3\text{CH}_2\text{-O-CHF}_2$ , 5.2; cyclo- $\text{CF}_2\text{CHFCF}_2\text{-O}$ , 26; cyclo- $(\text{CF}_2)_3\text{-O}$ , >330.

## Introduction

Because of the concerns regarding the role of chlorofluorocarbons (CFCs) in ozone depletion and greenhouse warming, partially fluorinated ethers are now being considered as CFC replacements in industrial applications. Since these compounds contain neither chlorine nor bromine, they do not contribute to ozone depletion, but still they must be evaluated as possible greenhouse gases. The assessment of the greenhouse warming potential of any compound requires an accurate determination of its atmospheric lifetime, which, for many species, is dictated largely by the rate of reaction with the hydroxyl (OH) radical in the troposphere. Presently, there is very little experimental information on the OH reactivity of fluorinated ethers. We have

therefore measured the rate constants for the reactions of OH with a representative group of hydro fluoro ethers and have used the results to estimate their tropospheric lifetimes by means of a comparison with the reactivity of  $\text{CCl}_3\text{CH}_3$ . The rate constant data also provide preliminary information on the effects of fluorine substitution on OH/ether reactivities, which may help in predicting the rate constants for reactions of other hydro fluoro ethers with OH.

## Experimental Section

Rate measurements were conducted at 296 K by the flash photolysis resonance fluorescence technique.<sup>1-3</sup> A pyrex reaction cell (100 cm<sup>3</sup> volume) was used in the flow mode. Reaction mixtures containing the hydro fluoro ether,  $\text{H}_2\text{O}$ , and Ar were prepared manometrically in glass storage bulbs and slowly flowed

<sup>†</sup>Contribution of the National Institute of Standards and Technology.

TABLE I: Rate Constants for the Reactions of OH with Partially Fluorinated Ethers at 296 K

ether	$k$ , cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>		$\tau^a$
	4.6 kV	3.3 kV	
CF <sub>3</sub> -O-CH <sub>3</sub>	$(2.14 \pm 0.15) \times 10^{-14}$		3.0
CF <sub>3</sub> -O-CHF <sub>2</sub>	$(3.38 \pm 0.41) \times 10^{-15}$	$(3.56 \pm 0.62) \times 10^{-15}$	19
CHF <sub>2</sub> -O-CHF <sub>2</sub>	$(2.53 \pm 0.24) \times 10^{-14}$	$(2.41 \pm 0.16) \times 10^{-14}$	2.6
CF <sub>3</sub> CH <sub>2</sub> -O-CH <sub>3</sub>	$(6.24 \pm 0.67) \times 10^{-13}$		0.1
CF <sub>3</sub> CH <sub>2</sub> -O-CHF <sub>2</sub>	$(1.25 \pm 0.09) \times 10^{-14}$	$(1.20 \pm 0.16) \times 10^{-14}$	5.2
cyclo-CF <sub>2</sub> CHFCF <sub>2</sub> -O	$(2.51 \pm 0.35) \times 10^{-15}$	$(2.40 \pm 0.30) \times 10^{-15}$	26
cyclo-(CF <sub>2</sub> ) <sub>3</sub> -O	$<2 \times 10^{-16}$		>330

<sup>a</sup> Approximate tropospheric lifetime for removal by OH, in years.

through the cell at a total pressure of 4.7 kPa (35 Torr) with a flow rate of 0.36 cm<sup>3</sup> s<sup>-1</sup> at STP. The argon diluent gas had a manufacturer's stated purity of  $\geq 99.998\%$  and was used without further purification.

The sample of CHF<sub>2</sub>OCHF<sub>2</sub>, provided by W. R. Grace & Co., was 99.35% pure with CHF<sub>2</sub>CH<sub>2</sub>F the major impurity as determined by gas chromatographic analysis. The samples of CF<sub>3</sub>OCH<sub>3</sub>, cyclo-CF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>O, and cyclo-CF<sub>2</sub>CHFCF<sub>2</sub>O were prepared by J. L. Adcock of the University of Tennessee and purified by gas chromatography. No impurities were detected by capillary GLC on a 60-m methylsilicone column, indicating a purity level of much greater than 99%. For CF<sub>3</sub>OCH<sub>3</sub>, the most likely impurity is CH<sub>3</sub>OCH<sub>3</sub>, while for the perfluorinated cyclic ether the most likely impurity is the monohydro analog and for the monohydro cyclic ether, the most likely impurity is the perfluorinated analog. Since CH<sub>3</sub>OCH<sub>3</sub> is likely to be much more reactive than CF<sub>3</sub>OCH<sub>3</sub>, we have analyzed the CF<sub>3</sub>OCH<sub>3</sub> sample further by mass spectrometry. The magnitude of the CH<sub>3</sub>OCH<sub>3</sub> parent peak,  $m/e$  46, is less than 1/7500 the magnitude of the parent of CF<sub>3</sub>OCH<sub>3</sub> at  $m/e$  100. Even this small amount is probably due at least partly to impurities in the mass spectrometer sampling system. Peaks at  $m/e$  143 (0.5% of  $m/e$  100) and 128 (0.2%) were also observed but not identified.

The sample of CF<sub>3</sub>OCF<sub>2</sub>H was supplied by D. DesMarteau of Clemson University, taken from a cylinder obtained from PCR, Inc. The sample was analyzed in DesMarteau's laboratory by both GLC and NMR. The total purity was 97.06% (NMR) or 97.34% (GLC) with the major impurity CF<sub>3</sub>OCF<sub>2</sub>F<sub>3</sub>, 2.17%, followed by CF<sub>3</sub>OCF<sub>3</sub>,  $\leq 1.68\%$ , and CF<sub>3</sub>OOFCF<sub>3</sub>, 0.32%.

CF<sub>3</sub>CH<sub>2</sub>OCHF<sub>2</sub> and CF<sub>3</sub>CH<sub>2</sub>OCH<sub>3</sub> were supplied by Halocarbon Corp. and had stated purity levels of  $>99.9\%$ , with the most likely impurity expected to be trifluoroethanol.

The OH radicals were produced by the flash photolysis ( $\lambda \geq 165$  nm) of 23 Pa (0.17 Torr) of H<sub>2</sub>O and monitored after the flash by OH resonance fluorescence at 308 nm. The latter was excited by a microwave-powered OH resonance lamp [130 Pa (1 Torr) of He saturated with water vapor]. The fluorescence decay was recorded on a microcomputer-based multichannel scaler as a summation of multiple flash photolysis experiments. The OH decay curves were then analyzed using a weighted linear least-squares routine ( $\ln$  (fluorescence signal) vs  $t$ ) to derive the first-order decay rate. Several such determinations were made at each set of experimental conditions. Due to the wide range in reactivity, ether concentrations ranged from  $3 \times 10^{14}$  to  $8 \times 10^{16}$  cm<sup>-3</sup>. In all cases, the concentration of the ether was in large excess ( $[OH] \leq 10^{10}$ – $10^{11}$  cm<sup>-3</sup>) so that first-order kinetic behavior applied to the OH radical disappearance and the signal exhibited an exponential decay. Decay rate constants were determined for several reactant concentrations and the second-order rate constants were derived from weighted linear least-squares fits of plots of first-order decay rate vs reactant concentration.

## Results and Discussion

The rate constants determined in this work are presented in Table I. For several of the compounds, rate constants were measured at flash threshold voltages of both 4.6 and 3.3 kV, corresponding to a difference of about a factor of 2 in the flash intensity. These measurements examine for possible contributions to the OH decay due to its reactions with photolysis or primary

TABLE II: Comparison of the Effects of F Substitution on the Reactivity toward OH between Hydrofluoroalkanes and Hydro Fluoro Ethers

compound	$k$ , cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	
	$k$ , cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$k$ , per C-H, cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>
CH <sub>4</sub> <sup>a</sup>	$6.5 \times 10^{-15}$	$1.6 \times 10^{-15}$
CH <sub>3</sub> F <sup>a</sup>	$1.8 \times 10^{-14}$	$6.0 \times 10^{-15}$
CH <sub>2</sub> F <sub>2</sub> <sup>a</sup>	$1.0 \times 10^{-14}$	$5.0 \times 10^{-15}$
CHF <sub>3</sub> <sup>a</sup>	$2.1 \times 10^{-16}$	$2.1 \times 10^{-16}$
CH <sub>3</sub> CH <sub>3</sub> <sup>a</sup>	$2.8 \times 10^{-13}$	$4.7 \times 10^{-14}$
CHF <sub>2</sub> CHF <sub>2</sub> <sup>a</sup>	$5.7 \times 10^{-15}$	$2.9 \times 10^{-15}$
CF <sub>3</sub> CHF <sub>2</sub>	$1.9 \times 10^{-15}$	$1.9 \times 10^{-15}$
CF <sub>3</sub> CH <sub>3</sub> <sup>a</sup>	$1.4 \times 10^{-15}$	$4.7 \times 10^{-16}$
CH <sub>3</sub> -O-CH <sub>3</sub> <sup>b</sup>	$2.5 \times 10^{-12}$	$4.2 \times 10^{-13}$
CHF <sub>2</sub> -O-CHF <sub>2</sub> <sup>c</sup>		$1.3 \times 10^{-14}$
CF <sub>3</sub> -O-CHF <sub>2</sub> <sup>c</sup>		$3.4 \times 10^{-15}$
CF <sub>3</sub> -O-CH <sub>3</sub> <sup>c</sup>		$7.1 \times 10^{-15}$
cyclo-C <sub>3</sub> H <sub>6</sub> <sup>d</sup>	$1.1 \times 10^{-13}$	$1.9 \times 10^{-14}$
cyclo-C <sub>4</sub> H <sub>8</sub> <sup>d</sup>	$1.75 \times 10^{-12}$	$2.2 \times 10^{-13}$
cyclo-C <sub>3</sub> H <sub>6</sub> -O <sup>e</sup>	$1.0 \times 10^{-11}$	
cyclo-CF <sub>2</sub> CHFCF <sub>2</sub> -O <sup>c</sup>	$2.5 \times 10^{-15}$	$2.5 \times 10^{-15}$

<sup>a</sup> DeMore, W. B.; Sander, S. P.; Molina, M. J.; Hampson, R. F.; Kurylo, M. J.; Golden, D. M.; Howard, C. J. and Ravishankara, A. R. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling: Evaluation No. 10 of the NASA Panel for Data Evaluation. JPL Publication 92-20. <sup>b</sup> Reference 4. <sup>c</sup> This work. <sup>d</sup> Reference 7. <sup>e</sup> Dagaut, P.; Liu, R.; Wallington, T. J.; Kurylo, M. J. *J. Phys. Chem.* 1990, 94, 1881.

reaction products. At the lower voltage, the concentrations of OH, of the primary reaction products, and of any ether photolysis products are reduced by factors of 2. Rate constants derived under both flash energy conditions were identical within the statistical uncertainties, indicating the absence of any significant contribution to the measured OH decays from competing reactions.

Table II contains the room-temperature rate constants for several alkanes and hydrofluoroalkanes, and for two nonfluorinated ethers, along with some of the results from this study. Also included in Table II is the rate constant per C-H ( $k_H$ ) for each compound in which all the C-H bonds are identical; this is the appropriate measure for comparing reactivities of different compounds.

It is clear from the results in Tables I and II that the inclusion of one or more fluorine atoms in an ether dramatically changes its reactivity towards OH. We can discuss these effects in two complementary ways: First we compare the effects of fluorination on the C-H reactivity in alkanes and the corresponding ethers. Second, we compare the reactivities of the fluorinated and non-fluorinated ethers. The fundamental assumption in these comparisons is that the reactions of OH with the alkanes and ethers all proceed via a hydrogen abstraction mechanism.

It can be seen from Table II that the substitution of a fluorine for a hydrogen atom on methane activates the other C-H bonds toward abstraction. Two fluorines are slightly less activating than one, while three fluorines significantly deactivate the remaining C-H bond. If we assume that the same activating effects of mono- and difluoro substitution translate to the ethanes, we would expect  $k_H$  for CHF<sub>2</sub>CHF<sub>2</sub> to be greater than  $k_H$  for CH<sub>3</sub>CH<sub>3</sub>. The greater than 10-fold decrease in  $k_H$  (for CHF<sub>2</sub>CHF<sub>2</sub>), however, indicates that fluorine substitution deactivates C-H bonds on the

adjacent carbon atom in ethanes. The relative deactivating effect as a function of the extent of fluorine substitution can be seen by comparing the  $k_H$  of  $\text{CF}_3\text{CH}_3$  with  $\text{CH}_3\text{CH}_3$  and of  $\text{CF}_3\text{CHF}_2$  with  $\text{CHF}_2\text{CHF}_2$ . The activating effect on C-H bonds by fluorine substitution is overridden by the deactivating effect of the fluorines on the adjacent carbon.

As demonstrated in many earlier studies,<sup>4-6</sup> the inclusion of an ether linkage in an alkane activates the C-H bonds, an effect which is felt at a distance of up to four carbons from the ether functional group. For example, dimethyl ether is 8.9 times more reactive toward OH than ethane. Enhancements are also observed when fluorine-substituted dimethyl ethers are compared with the corresponding fluorine-substituted ethanes, although there seems to be some inconsistency in the magnitudes of the reactivity enhancement, as will be discussed later.

It is important to recognize that the reactivities of C-H bonds in a hydro fluoro ether cannot be accounted for simply by the additive effects of the -O- linkage and the F substituents. As we will see, fluorine substitution tends to lessen the activating effect of the ether function. First we consider F substitutions at the  $\alpha$  positions by comparing the  $k_H$ 's of  $\text{CF}_3\text{OCH}_3$  and  $\text{CF}_3\text{OCHF}_2$ . The reduction in  $k_H$  with difluoro substitution suggests that the activating effect exerted on the remaining C-H bond on the same carbon is more than compensated by a decrease in the activating effect of the -O- linkage. The net effect is such that  $k_H$  for  $\text{CF}_3\text{OCHF}_2$  is greater than that for  $\text{CF}_3\text{CHF}_2$  but a factor of 2 less than  $k_H$  for  $\text{CF}_3\text{OCH}_3$ .

The reduction of the activating effect of -O- as a result of F substitution seems to be felt by the  $\alpha$  C-H bonds on both sides of the -O- linkage. For example, the C-H bonds in  $\text{CF}_3\text{OCH}_3$  are nearly 60 times less reactive than those in  $\text{CH}_3\text{OCH}_3$ , although they are still 15 times more reactive than those in  $\text{CF}_3\text{CH}_3$ . In fact, a decrease in the activation by -O- may still be felt by the  $\alpha$  C-H bond even when the  $\text{CF}_3$  group is at the  $\beta$  position across the -O- linkage. If, in  $\text{CF}_3\text{CH}_2\text{OCH}_3$ , the C-H bonds of the  $\text{CH}_2$  group are as strongly deactivated by  $\text{CF}_3$  as the C-H bonds are in  $\text{CF}_3\text{CH}_3$ , then most of the reactivity in  $\text{CF}_3\text{CH}_2\text{OCH}_3$  would be associated with the terminal C-H's of the  $\text{CH}_3$  group. Even under this extreme assumption, the reactivity per C-H of this terminal  $\text{CH}_3$  is only 50% of the  $k_H$  in  $\text{CH}_3\text{OCH}_3$ , suggesting a decrease in the activating effect of the ether functional group due to the presence of the  $\beta$   $\text{CF}_3$  across the -O- linkage. Any reactivity contribution due to the  $\text{CH}_2$  group in  $\text{CF}_3\text{CH}_2\text{OCH}_3$  would lessen the  $k_H$  of the terminal  $\text{CH}_3$  even further.

A final comparison can be made for cyclo- $\text{CF}_2\text{CHFCH}_2\text{O}$ , which is the only hydro fluoro ether in the present investigation that has no  $\alpha$  C-H bond but one C-H bond  $\beta$  to the ether function. The  $k_H$  for this compound is between 2 and 3 orders of magnitude lower than the reactivity in cyclo- $\text{CH}_2\text{CH}_2\text{OCH}_2$ . It is also 7.6 and 88 times less reactive than the C-H bonds in cyclo- $\text{C}_3\text{H}_6$  and cyclo- $\text{C}_4\text{H}_8$ , respectively.<sup>7</sup> Clearly the  $\text{CF}_2$  groups have an exceptionally strong negative influence on the C-H adjacent to them both and any activation by the ether linkage is completely suppressed.

Although the above (largely qualitative) analysis explains some of the reactivity patterns of the ethers, there are some reactivity changes that cannot be explained readily. For example, a comparison of the OH rate constants for  $\text{CH}_3\text{OCH}_3$  and  $\text{CH}_3\text{CH}_3$  shows that -O- activates the adjacent C-H bonds by a factor of 8.9. Similarly, the activation factor for  $\text{CHF}_2\text{OCHF}_2$  over  $\text{CHF}_2\text{CHF}_2$  is found to be 4.5. In the case of  $\text{CF}_3\text{OCHF}_2$  and  $\text{CF}_3\text{CHF}_2$ , the factor drops to 1.7, demonstrating a greatly reduced activating effect with increasing fluorine substitution. It is most surprising, however, to find that the activation factor for  $\text{CF}_3\text{OCH}_3$  over  $\text{CF}_3\text{CH}_3$  equals 15 (substantially greater than that for the nonfluorinated analogues). It is difficult to explain such a difference even on a qualitative basis. Clearly, more experimental data, particularly on the temperature dependence, are needed in order to fully understand the reactivity changes associated with fluorine substitution.

An attempt has been made to predict the rate constants for the reactions of OH with hydro fluoro ethers using the structure-

activity relationship (SAR) values from Atkinson,<sup>8</sup> with very little success. For example,  $\text{CF}_3\text{OCF}_2\text{H}$  is predicted to be 32 times more reactive than measured, while cyclo- $\text{CHFCH}_2\text{OCF}_2$  is predicted to be 11 times less reactive than measured. Attempts to use the new experimental data to derive new group values by the same procedure as used by Atkinson have also proven to be unsuccessful. This is undoubtedly due to the fact that the SAR approach includes only next-neighbor interactions in the derivation of the group values. Clearly, long-range effects of fluorine substitution are important in determining the reactivity of such compounds and must be considered in developing semiempirical estimation procedures.

In addition to the partially fluorinated ethers, the present investigation also included the fully fluorinated cyclo- $(\text{CF}_2)_3\text{O}$ . Although this compound contains no abstractable hydrogen atoms, there was a small possibility that OH might add to the ether linkage, particularly under conditions of significant ring strain. Our experiments indicated the absence of any measurable reactivity and hence we are able to place an upper limit on the rate constant. Clearly, the addition mechanism is not important for this compound.

Included in Table I are estimated lifetimes for removal by tropospheric OH, calculated by comparison with  $\text{CH}_3\text{CCl}_3$ . This comparison assumes that reaction with OH is the dominant tropospheric loss mechanism for both the ethers and  $\text{CH}_3\text{CCl}_3$  and, hence, is useful only in a semiquantitative manner to compare the relative lifetimes of species for which the atmospheric photochemistry is similar. Exact lifetime calculations are best performed using a full atmospheric photochemical model. The tropospheric lifetime of  $\text{CH}_3\text{CCl}_3$  was calculated to be 7.0 years from the total lifetime of 5.7 years<sup>9</sup> corrected for the estimated 85-year lifetime due to ocean loss and for the 47-year lifetime calculated for stratospheric loss.<sup>10</sup> In the tropospheric lifetime calculations, we used the rate constant for  $\text{CH}_3\text{CCl}_3$  at 296 K ( $9.3 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ),<sup>11</sup> since the present measurements were carried out only at room temperature. Although more accurate lifetime estimates are obtained<sup>12</sup> by using the rate constants at 277 K, the use of the  $k_{296}$  values is valid if the temperature dependence of the other reaction is not dramatically different from that of the  $\text{CH}_3\text{CCl}_3$  reaction.

The tropospheric lifetimes of the hydrofluoroethers calculated in this manner range from 0.1 to 26 years. For  $\text{CF}_3\text{CH}_2\text{OCH}_3$ , the shortest-lived compound, the calculation is probably not valid since it is not expected to be well mixed in the global troposphere. Hence, the tropospheric removal rate of this ether is likely to be controlled by regional effects. Its high reactivity, however, suggests that it will be removed rapidly and that the chemical identity and fate of the reaction products require further study. For the very long-lived ethers, concerns over appreciable atmospheric accumulation require that removal mechanisms other than gas-phase reaction with OH need to be fully delineated. The extremely long lifetime calculated for removal by OH for the fully fluorinated cyclo- $(\text{CF}_2)_3\text{O}$  clearly indicates that other loss mechanisms, such as transport into the stratosphere, will dominate for this ether.

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## Gas-Phase Chemiluminescence Study of Chemically Activated Tetramethyl-1,2-dioxetane Formed from the Reaction of $O_2(^1\Delta_g)$ with 2,3-Dimethyl-2-butene

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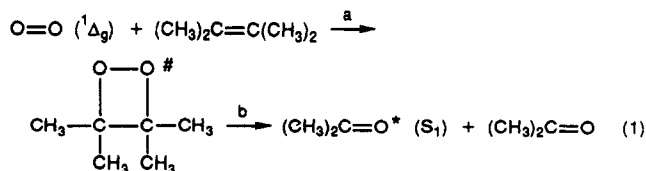
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Chemically activated tetramethyl-1,2-dioxetane has been prepared by the reaction of  $O_2(^1\Delta_g)$  with 2,3-dimethyl-2-butene at temperatures of 450 to 775 K and a pressure of 0.25 Torr. The observed product of the reaction was excited  $^1n\pi^*$  ( $S_1$ ) acetone, which was identified by chemiluminescence spectra of the acetone ( $S_1 \rightarrow S_0$ ) transition. Neither acetone ( $T_1$ ) nor any other excited states were observed under the above conditions. The temperature dependence of the chemiluminescence gave an activation energy for the cycloaddition reaction of  $8610 \pm 200$  (1 $\sigma$ ) cal/mol. The quantum yield for acetone ( $S_1$ ) was  $4 \times 10^{-3}$  per reactive collision; its (1 $\sigma$ ) error is estimated as  $\pm$  a factor of 3. Chemiluminescence spectra taken at  $O_2(^3\Sigma_g^-)$  partial pressures greater than 2 Torr showed formaldehyde ( $S_1 \rightarrow S_0$ ) bands. This is attributed to the well-known hydrocarbon "cool flame" mechanism, due to the presence of methyl radical formed by the thermal decomposition, in two steps, of 2,3-dimethyl-3-hydroperoxy-1-butene, another product path for the title reaction. This is the first report on the chemically activated decomposition of tetramethyl-1,2-dioxetane.

### Introduction

The decompositions of 1,2-dioxetanes have been widely studied because these interesting processes yield electronically excited singlet- and triplet-state carbonyl compounds as products.<sup>1-13,19,21a,22</sup> Tetramethyl-1,2-dioxetane (TMD) is the prototype, and by far the most studied, molecule in this class. The vast majority of the many previous investigations of TMD have been devoted to the *thermal decomposition* in solution. In contrast, we report the *first* study of *chemically activated* TMD prepared by the gas-phase cycloaddition of  $O_2(^1\Delta_g)$  with tetramethylethene (TME), reaction 1,



where # denotes vibrational excitation and \* denotes electronic excitation. The lack of prior data stems from the fact that most olefins having allylic hydrogen react preferentially with  $O_2(^1\Delta_g)$  to form allylic hydroperoxide.<sup>13-15</sup> The reactants  $O_2(^1\Delta_g)$  and tetramethylethene (TME) are believed to be capable of forming tetramethyl-1,2-dioxetane,<sup>13</sup> but prior to the present work no evidence for this had been reported. These reactants are known to form the allylic hydroperoxide 2,3-dimethyl-3-hydroperoxy-1-butene,<sup>26</sup> with a low activation energy.<sup>14,15</sup> Through careful control of the reaction conditions we have observed the dioxetane pathway, reaction 1, and measured the CL activation energy and the quantum yield of acetone  $S_1$  product.

The *chemical activation* transition state contains significantly more internal energy than the *thermal decomposition* transition state. This important difference is apparent upon inspection of the reaction coordinate diagram. Figure 1 was constructed by using bomb calorimetry data on the enthalpy of formation of TMD<sup>16</sup> and other thermochemical and photochemical data.<sup>41</sup> The activation energy,  $E_{1a}$ , was taken from the present work. The local maximum of energy labeled  $TS_{1a}$  is the *chemical activation* transition state, located 26 kcal/mole above  $TS_{1b}$ , the *thermal decomposition* transition state. Both transition states are connected to the electronic ground state of TMD, shown in the center of Figure 1.

Excited carbonyls have been observed by chemiluminescence in studies of the gas-phase reactions of  $O_2(^1\Delta_g)$  with various olefins and were attributed to the formation and subsequent decomposition of *chemically activated* dioxetanes by clean bimolecular cycloaddition reactions.<sup>8,9,22</sup> The initially formed dioxetanes were claimed to be vibrationally excited by an amount that in Figure 1 corresponds to the quantity  $(E_{1a} - \Delta H_{1a}) = 52$  kcal/mol. It is particularly significant that the CL activation energies that we have found in previous experiments done in bulk gas<sup>8</sup> are close to the threshold translational energies required to observe CL in crossed molecular beams under single-collision conditions.<sup>9</sup> Conducting olefin plus  $O_2(^1\Delta_g)$  reactions in solution leads to dioxetane molecules with thermal Boltzmann energy distributions because collisions with solvent molecules deactivate the initial adducts. Several such solution-phase studies of singlet oxygenation reactions have reported spectroscopic evidence for the presence of dioxetane products.<sup>11,12</sup>

Dioxetane rings with many different substituents on carbon atoms 3 and 4 have been prepared and subjected to *thermal*