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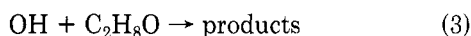
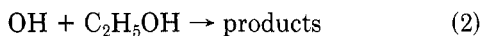
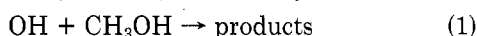
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Kinetic Rate Constants for the Reaction of OH with Methanol, Ethanol, and Tetrahydrofuran at 298 K

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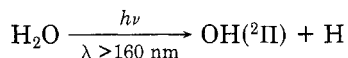
Sir: In the past few years, in an effort to understand the chemistry of the lower atmosphere, OH radical reactions with paraffinic, olefinic, and aromatic hydrocarbons have been extensively studied; however, very little data are available on oxygenated hydrocarbons. Methanol, ethanol, and tetrahydrofuran (THF) are widely used as industrial solvents and enter the troposphere through evaporation. The input of alcohols in urban air could increase further if they are used in internal combustion engines. We report here the results from a kinetics study of the reactions of OH with methanol, ethanol, and tetrahydrofuran.



The rate coefficient for reaction 1, k_1 , has been previously measured by Overend and Paraskevopoulos¹ ($k_1 = 1.06 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), Campbell et al.² ($0.94 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), and Osif et al.³ ($0.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). The first two investigators have also measured k_2 as 3.7×10^{-12} and $3.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. The only one reported value for the rate coefficient of reaction 3 is that of Winer et al.⁴ who obtained a value of $1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ using an environmental chamber.

The technique of flash photolysis-resonance fluorescence, employed in this investigation, has been thoroughly documented in the literature and will not be further described here.⁵⁻⁷ Only those details that are necessary for an understanding of the present study have been expanded.

OH radicals were produced by photolyzing H_2O with vacuum UV light transmitted through a quartz window.



After a delay of 100 μs following the photolysis, the OH radical decay was measured via resonance fluorescence. All experiments involving reactions 1-3 were carried out under pseudo-first-order conditions with OH being the minor species, i.e., $[\text{CH}_3\text{OH}]/[\text{OH}] > 300$, $[\text{C}_2\text{H}_5\text{OH}]/[\text{OH}] > 75$, $[\text{THF}]/[\text{OH}] > 30$. Since many flashes were typically required to develop a smooth decay curve, a given gas reaction mixture was replaced approximately every 60 flashes. In this case the percentage of decomposition was <3%.

TABLE I: Rate Constant Measurements for Reactions of OH with Methanol and Ethanol at 298 K^a

CH_3OH , mtorr	flash energy, J	flashes/ filling	k_1' , s^{-1}	$10^{12}k_{\text{bi}}$, cm^3 $\text{molecule}^{-1} \text{ s}^{-1}$
0.0	88	50	40	
2.0	88	50	109	
4.0	88	50	167	
6.0	88	50	251	
6.0	88	100	214	
6.0	245	50	238	
8.0	88	50	288	
10.0	88	50	373	(1.00 ± 0.10)

$\text{C}_2\text{H}_5\text{-OH}$, mtorr			k_2' , s^{-1}	
0.0	88	50	49	
0.5	88	50	102	
1.0	88	50	142	
1.5	88	50	184	
1.5	245	50	216	
1.5	88	100	195	
2.0	88	50	214	
2.5	88	50	263	(2.62 ± 0.36)

^a All experiments were carried out with 200 mtorr of H_2O and 40 torr of He. All quoted errors are 2σ .

A MKS Baratron and a two-turn Bourdan gauge (Wallace and Tiernan Type FA145) were used to measure low (1-3000 mtorr) and high pressures (800 torr), respectively. The precision with which reaction gas mixtures could be made up was ~5%. Helium used in this study was Matheson grade with a stated purity of >99.9999%. Methanol, ethanol, and tetrahydrofuran were analyzed samples from Baker Chemical Co. All three of these reagents were degassed before use.

The results from the OH- CH_3OH and OH- $\text{C}_2\text{H}_5\text{OH}$ studies are shown in Table I. The bimolecular rate constants k_1 and k_2 were computed from the measured pseudo-first-order rate constants using a linear least-squares analysis. The quoted errors for both k_1 and k_2 are 2σ values which denote the precision of our measurements.

$$k_1 = (1.00 \pm 0.10) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_2 = (2.62 \pm 0.36) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

In previous kinetic investigations of OH reactions in our laboratory, under conditions similar to the present measurements, it has been demonstrated that radical-radical reactions such as H + OH and OH + OH were of negligible importance. Both modeling calculations as well as variations in the OH concentration have also shown that contributions from reactions such as OH + CH_3 and OH + C_2H_5 were of negligible importance (see Table I).

Our value of k_1 is in excellent agreement with the direct measurements of Overend and Paraskevopoulos⁴ ($1.06 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and the indirect derivations of Campbell et al.⁵ ($0.94 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). In sharp contrast, the value of k_1 reported by Osif et al.,⁶ $0.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,⁸ is in major disagreement with the k_1 values reported here.

Our reported value of k_2 is noticeably lower (~30%) than that obtained by both Overend and Paraskevopoulos⁴ ($3.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and Campbell et al.⁵ ($3.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). One probable source of the discrepancy between our work and that of Overend and Paraskevopoulos (the only direct measurement reported in the literature) is that the latter authors may have overestimated k_2 due to a significant reaction of OH with the photolysis products from ethanol. In the study by

TABLE II: Rate Constant Data for the OH + THF Reaction^a

He press., torr	THF, mtorr	flash energy, J	k_3' , s ⁻¹	$10^{11}k_{bi}$, cm ³ molecule ⁻¹ s ⁻¹
20	0	88	71	
	0.2	88	200	
	0.4	88	297	
	0.4	260	323	
	0.6	88	397	
	0.8	88	501	(1.63 ± 0.16)
200	0	88	53	
	0.2	88	182	
	0.4	88	243	
	0.6	88	325	
	0.8	88	516	(1.59 ± 0.39)

^a All experiments were carried out with 200 mtorr of H₂O and 60 flashes per filling. All quoted errors are 2σ. He was the diluent gas.

Overend and Paraskevopoulos very high concentrations of alcohol were employed. The other possible explanation for this discrepancy would be that there was some loss of C₂H₅OH in our system to the walls of the reactor, thereby resulting in a lower rate constant. With a quartz reactor, we do not believe that this is very likely.

The results from the OH-THF experiments are shown in Table II. As in the study of reactions 1 and 2, it was demonstrated that secondary reactions were of negligible importance in the OH-THF system. Variations in the diluent gas pressure of a factor of 10 clearly established the second-order kinetic behavior of this reaction (see

Table II). Thus, reaction 3 is most likely to be a hydrogen atom abstraction reaction since THF has no double bonds. Our value of k_3 is in excellent agreement with the indirect measurements of Winer et al.⁴ who obtained k_3 as 1.4×10^{-11} cm³ molecule⁻¹ s⁻¹.

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References and Notes

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