Absolute Rate Constant for the Reaction of O(³P) with Ethanol

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The rate constant for the reaction of atomic oxygen with ethanol was measured directly by two experimental techniques: flash photolysis-resonance fluorescence (FP-RF, 297-886 K) and discharge flow-resonance fluorescence (DF-RF, 298-706 K). Kinetic complications in the DF-RF experiments from a fast secondary reaction and heterogeneous effects were overcome by operating at very low initial O-atom concentrations combined with the addition of excess O_2 . Under these conditions results obtained in the DF-RF experiments were in very close agreement with those from the FP-RF work, which was not perturbed by any apparent complication. The combined results show slight non-Arrhenius behavior and the data were accordingly fit to a three-parameter expression, 298-886 K, $k_1(T) = 9.88 \times 10^{-19} T^{2.46} \exp(-932/T)$, in units of cm³ molecule⁻¹ s⁻¹, with an error limit of about $\pm 15\%$ over the given temperature range. In addition, initial [O] variation experiments were carried out at 298 K in the DF-RF apparatus to investigate the mechanism of this reaction, and model calculations for an assumed mechanism were performed. Finally, the branching ratios for the three possible H-abstraction channels are discussed in light of the non-Arrhenius behavior displayed in the present rate data.

Introduction

The reaction of atomic oxygen with ethanol

$$O(^{3}P) + C_{2}H_{3}OH \rightarrow CH_{3}CHOH (CH_{2}CH_{2}OH, CH_{3}CH_{2}O) + OH (1)$$

is but one of many elementary steps that comprise the complex chemical kinetic scheme of the combustion of ethanol and ethanol-blended fuels. The relative importance of reaction 1 in the overall mechanism remains in doubt, however, since the rate coefficient $k_1(T)$ is not unambiguously known, even at ambient temperature. The pioneering work of Kato and Cvetanovic¹ yielded a rate coefficient of $k_1(298) = 1.25 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1}$ s^{-1} in competition with O(³P) + 1-butene. Other early results on k_1 are not recommended in the evaluation by Herron and Huie.² In a more recent flow reactor study, Owens and Roscoe³ investigated k_1 in the absence of O_2 as well as with O_2 excess. The respective k_1 values differed by roughly a factor of two and could be brought into coincidence by the application of stoichiometry factors. This result was later⁴ multiplied by another correction factor of 1.6 to yield $k_1(298) = 8.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

The work of Roscoe and co-workerrs^{3,4} suggests that under their conditions a complex mechanism prevails. A similar conclusion may be drawn from the flow tube work of Faubel.⁵ After corrections for stoichiometry she obtained values of $k_1(298) = 7.7$ \times 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ under conditions of ethanol excess and $2.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ under conditions of O-atom excess.}$

The bandwidth of ambient temperature results for the rate constant of reaction 1 is increased further and toward a larger value by the recent flow reactor study of Washida,⁶ who reported $k_1(298) = (1.7 \pm 0.3) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ under O-atom}$ excess conditions.

On the other hand, a "low" ambient temperature rate coefficient for $O(^{3}P) + C_{2}H_{5}OH$ seems more plausible by comparison to $O(^{3}P) + CH_{3}OH$. The ambient temperature rate coefficient for the latter reaction was found by Klemm and co-workers⁷ to be $k(298) = 5.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ under conditions free from}$ subsequent reactions, contrary to the then accepted value of k(298)= 2.5×10^{-14} cm³ molecule⁻¹ s⁻¹. In a concurrent study⁸ it was shown that the erroneously high rate data on $CH_3OH + O$ were caused by O-atom consumption via the chain

 $O + CH_2OH \rightarrow CH_2O + OH$

$$OH + CH_1OH \rightarrow CH_2OH + H_2O$$

If a similar mechanism would apply also in the case of C_2H_5OH

+ O, it would decrease the wide gap between $CH_3OH + O$ and $C_2H_5OH + O$ reactions, respectively. It also would explain some of the complications in the previous studies. Of course, the contribution of such a mechanism may vary with temperature. Thus, the measurement of the activation energy of the primary reaction, E_{a1} , may be obscured. Only one value for E_{a1} is available in the literature; it was reported by Owens and Roscoe³ and refers to the narrow temperature range between 301 and 439 K. Moreover that result depended on a stoichiometry factor that was assumed to be independent of temperature. For these reasons this E_{a1} value of Owens and Roscoe should be taken with care.

The objective of the present work is threefold: (1) determine the temperature dependence of the rate constant, k_1 , using direct techniques; (2) investigate the effect of subsequent reactions that might have obscured earlier studies; and (3) compare the mechanisms for $CH_3OH + O$ and $C_2H_5OH + O$.

Experimental Section

The two direct techniques utilized in this kinetic study of reaction 1 were the flash photolysis-resonance fluorescence method (FP-RF)^{9,10} and the discharge flow-resonance fluorescence method (DF-RF).^{11,12} Both techniques were employed over a wide range in temperature: FP-RF, 297-886 K; DF-RF, 298-706 K.

The DF-RF apparatus has been described in detail previously.¹² The only change was in the design of the resonance lamp to achieve greater detection sensitivity for O atoms. This new design simply involved the use of 6-mm tubing for the lamp body instead of the normal 12-mm size. With this change it was necessary to fabricate the lamp so that the 1/4-wave microwave cavity was offset to bring the antenna in proximity of the 6-mm tubing wall, i.e., the 6-mm lamp body was not coaxial with the cavity. With this minor change

- (2) Herron, J. T.; Huie, R. E. J. Phys. Chem. Ref. Data 1973, 2, 467. (3) Owens, C. M.; Roscoe, J. M. Can. J. Chem. 1976, 54, 948.
- (4) Ayub, A. L.; Roscoe, J. M. Can. J. Chem. 1979, 57, 1269.

- (4) Ayub, A. L.; Roscoe, J. M. Can. J. Chem. 1979, 57, 1269.
 (5) Faubel, C. Dissertation, University of Göttingen, 1977.
 (6) Washida, N. J. Chem. Phys. 1981, 75, 2715.
 (7) Keil, G. D.; Tanzawa, T.; Skolnik, E. G.; Klemm, R. B.; Michael, J. V. J. Chem. Phys. 1981, 75, 2693.
 (8) Grotheer, H.-H.; Just, Th. Chem. Phys. Lett. 1981, 78, 71.
 (9) Braun, W.; Lenzi, M. Chem. Soc. Faraday Discuss. 1967, 44, 252.
 (10) Klemm, R. B. J. Chem. Phys. 1979, 71, 1987. Klemm, R. B.; Stief, L. J. J. Chem. Phys. 1974, 61, 4900, and references therein.
 (11) Clyne, M. A. A.; Cruse, H. W. J. Chem. Soc., Faraday Trans. 2 1972, 68, 1281. Bemand, P. P.; Clyne, M. A. A. J. Chem. Soc., Faraday

Trans. 2 1973, 69, 1643. (12) Klemm, R. B.; Skolnik, E. G. Presented at the 177th National

Meeting of the American Chemical Society, Honolulu, HI, April, 1979, Abstract BNL-25192. Klemm, R. B.; Skolnik, E. G.; Michael, J. V. J. Chem. Phys. 1980, 72, 1256, and references therein.

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⁽¹⁾ Kato, A.; Cvetanovic, R. J. Can. J. Chem. 1967, 45, 1845.

in lamp design, the O-atom detection sensitivity was increased by a factor of three to about 7×10^5 atoms cm⁻³ count⁻¹ (30 s)⁻¹. At signal/noise ≈ 1 , this corresponds to a detection limit of [O] $\simeq 3 \times 10^8$ atoms/cm³. Experiments were thereby routinely performed using initial O-atom concentrations of about $(1-2) \times$ 10^{10} atoms/cm³. The calibration curve used to determine the sensitivity is presented in Figure 1. This calibration was performed, using the well-known N + NO titration reaction, with excess N atoms; thus $[O] \simeq [NO]$.

The FP-RF apparatus used in this work has been described in detail previously.¹⁰ The only significant change was the use of a quartz reaction cell. This new cell was fabricated entirely from quartz and was fitted with air-cooled optical ports. The cell was heated by platinum resistance wire with an inner winding (directly on the cell) and an outer winding that were separated by insulating, high-temperature fabric (Fiberfrax, Inc.). The entire assembly was wrapped with several layers of insulating material to achieve adequate temperature control. The cell was clamped to the top of the flash lamp/filter chamber assembly and separated from the filter chamber with a 1-in.-diameter magnesium fluoride window. All the ports on the cell were fitted with quartz O-ring joints that were thermally isolated from the cell via built-in, air-cooled quartz flanges. The resonance lamp port and the photomultiplier port were fitted with adapter flanges that allowed dry nitrogen to be used to purge the gap between each device and the isolation windows. The windows in this case were replaced with vacuum-UV lenses fabricated from magnesium fluoride (Harshaw); the focal lengths at 1302 Å were approximately 3.5 cm for the lens on the photomultiplier port and 10 cm for that on the resonance lamp port. Using this lens arrangement improved signal and increased the signal to background ratio by about a factor of three over that achieved with simple flat windows.

The FP-RF experiments were performed in the usual way¹⁰ with preformed gas mixtures of O₂ or NO and ethanol in argon diluent. O_2 was used as the O-atom photolytic source at four temperatures between 297 and 766 K; and NO was used at two temperatures, 514 and 886 K. The wavelength cutoffs of the windows employed on the photoflash were ~ 160 nm (Suprasil quartz) for O₂ and \sim 145 nm (sapphire) for NO.

All of the gases used in this work, except NO, were of the highest purity obtainable and were used directly from cylinders without further purification. The oxygen (99.999%), argon (99.9999%), and helium (99.9999%) were MG scientific grade at the indicated purity levels. The nitric oxide (Matheson, 99.0%) was purified by outgassing at 77 K and vacuum distilling (several times) from 175 (methanol slush) to 77 K with about an 80% yield. The ethanol (U.S. Industrial Chemicals Co., 200 proof, dehydrated, USP, punctilius) was analyzed initially by FTIR and the only detectable impurity above a few ppm was CO₂, at about 2%. This CO₂ impurity was effectively removed by pumping on the liquid ethanol sample that was repeatedly warmed to a temperature somewhat above ambient (50-60 °C). It was necessary to apply this procedure until about one-half of the ethanol had been evaporated off, in order to reduce the CO₂ contamination to a level below 100 ppm.

Results

Rate Constant Measurement. Kinetic data were obtained with ethanol in large excess over that of atomic oxygen $([C_2H_5OH]/[O]_0 > 10^4$ at ambient temeprature, and always >10² at higher temperatures), so that O-atom removal by reaction 1 was always pseudo-first order.

With the DF-RF method, the decay of O atoms is given by

$$\ln [O] = -k_{obsd}(d/v) + \ln [O]_0$$
(I)

where [O] is proportional to the fluorescence signal, d is the distance from the reactant injector probe tip to the detector, and v is the linear flow velocity. Linear decays obtained from eq I are shown in Figure 2a for data at 298 K and in Figure 2b for data at 445 K. The experimental first-order decay constant, K_{obsd} , was obtained by linear least-squares analyses of first-order plots



Figure 1. Calibration curve for oxygen atom detection by resonance fluorescence. O atoms were produced by the fast reaction of NO in an excess of N atoms. The temperature of the flow tube was 752 K, while the temperature of the fluorescence scattering cell was 321 K. All flow and concentration calculations were made for T = 321 K. The main carrier gas was helium, as usual, and a mole fraction of about 0.08 for N_2 was used to produce $[N] = 10^{14}$ atoms/cm³. Other conditions were v = 1380 cm/s and $P_T = 2.78$ Torr. The solid line represents a linear least-squares evaluation of eight measurements with [NO] (\approx [O]) ranging from 9×10^{10} to 1.6×10^{12} molecules/cm³ which gives a sensitivity factor for O-atom detection of 7.5×10^5 atoms cm⁻³ count⁻¹ (30) s)⁻¹.

according to eq I. The diffusion-corrected first-order constant, $K_{\rm c}$ was then calculated from¹³

$$K_{\rm c} = K_{\rm obsd} (1 + K_{\rm obsd} D / v^2) \tag{II}$$

where D is the diffusion coefficient for O atoms in helium. Replacement of D by an effective diffusion coefficient, $^{14} D_{eff}$, in order to account for the effect of Poiseuille flow does not change our correction for K_{obsd} significantly throughout the range of conditions.

The biomolecular rate coefficient, k_1 , is related to K_c through the expression

$$K_{\rm c} = k_1 [C_2 H_5 OH] + \Delta K_{\rm w} \tag{III}$$

where ΔK_w is the difference between the O-atom wall termination constant for the region downstream of the probe tip, K_{w1} , and that for the region uptstream of the probe tip, K_{w2} . The bimolecular rate coefficient was determined from linear least-squares analyses of the data according to eq III. Typical data sets at 298 and 445 K are shown in Figure 3. The results for the DF-RF are given in Table I.

Experiments were performed using low [O]₀ to avoid secondary reactions as pointed out in more detail in the next section. The DF-RF experiments were performed over the temperature range 298-706 K. At 298 K a teflon coating was used to minimize the wall loss of O atoms. At higher temperatures, the quartz reactor was treated with a 10% HF solution,¹⁵ and excess O₂ was used to eliminate heterogeneous effects.⁷

It is noted that the intercepts in Table I, ΔK_{w} , are statistically larger than zero, except those at ambient temperature for which the teflon-coated flow tube was used. The reason for these large intercepts, in the presence of excess O_2 and with an uncoated quartz flow tube, might be a minor heterogeneous (wall) reaction. Even so, the significance of the larger than normal $\Delta K_{\rm w}$ values is small primarily because the first-order rate constants were made large, and the K_c values covered a wide range (typically a factor of 5 to 8).

Atom decays from the real-time FP-RF experiments follow the relation

$$\ln [O]_0 / [O]_t = Kt$$
 (IV)

$$K = K_{\rm D} + k_1 [\rm C_2 H_5 OH]$$
 (V)

⁽¹³⁾ Kaufman, F. Prog. React. Kinet. 1961, 1, 1.

 ⁽¹⁴⁾ Kaufman, F. J. Phys. Chem. 1984, 88, 4909.
 (15) Klemm, R. B.; Tanzawa, T.; Skolnik, E. G.; Michael, J. V. Proc. Symp. (Intl.) Combust., [Proc.], 18th 1981, 785-799.



Figure 2. Typical first-order decays for O atoms from the reaction O(³P) + C₂H₅OH: A, T = 298 K, $P_T = 1.75$ Torr, v = 1227 cm/s. Ethanol concentrations are as follows: \bullet , 1.27 × 10¹⁵; O, 6.7 × 10¹⁴; \otimes , 2.75 × 10¹⁴. Units are molecules/cm³. B, T = 455 K, $P_T = 2.53$ Torr, v = 1878 cm/s. Ethanol concentrations are as follows: \Box , 7.25 × 10¹⁴; \blacksquare , 3.54 × 10¹⁴; \blacksquare , 1.01 × 10¹⁴. Units are molecules/cm³.

where $[O]_i$ is the O-atom concentration at time = t following the photoflash; $[O]_0$ is the initial O-atom concentration; K is the experimental first-order decay rate for reaction and "diffusion"; and K_D is the combined depletion rate for O atoms due both to reaction with O_2 (+M) or NO (+M) and to diffusion from the reaction viewing zone. The "diffusion" rate constant, K_D , was obtained in experiments that omitted ethanol from the gas mixture, and the bimolecular rate constant was derived from

$$k_1 = (K - K_D) / [C_2 H_5 OH]$$
 (VI)

The results from the FP-RF experiments were performed over the temperature range 297-886 K and are given in Table II. Table IIA contains results from experiments that used O_2 as the photolytic source of O atoms while Table IIB lists results where NO was the source. At 383 K, experiments were performed on gas mixtures where the O_2 concentration was varied by a factor of about seven. The values for k_1 derived from these experiments are in close agreement, thus negating the possibility of O-atom



Figure 3. Corrected first-order rates for reaction 1 vs. ethanol concentration. Data taken from Table I: \circ , T = 445 K; \bullet , T = 298 K.

re-formation in the experiments with high O_2 concentrations. This potential source of error was investigated further at high temperatures (Table IIB) in experiments that employed NO as the photolytic source of O atoms.

An Arrhenius plot of the combined DF and FP results from Tables I and II is shown in Figure 4. The agreement between these complementary techniques is quite good and this further demonstrates that the DF measurements were not significantly perturbed by possible heterogeneous (wall) effects. This plot exhibits a slight curvature and the data were fitted to the following analytical form

$$k_1(T) = 9.88 \times 10^{-19} T^{2.46} \exp(-932/T)$$
 (VII)

in units of cm³ molecule⁻¹ s⁻¹. The largest deviation of any data point from this fit is about 13% and thus an error limit of about $\pm 15\%$ may be taken over the temperature range 297 K < T < 886 K.

Mechanism at Ambient Temperature. The measurements to be described below have been carried out in order to gain some insight into the role of subsequent homogeneous reactions and thus provide at least a partial explanation for the discrepancies between this study and earlier ones. The DF-RF method was used to measure rate coefficients for O-atom consumption as a function of initial O-atom concentrations that were determined from the calibration curve (Figure 1). A systematic variation of $[O]_0$ was undertaken only at room temperature for two reasons: (1) In the related $O + CH_3OH$ system, heterogeneous effects have been observed under conditions similar to those for temperatures >450 K and have been suppressed by the addition of O_2 that somehow changed the wall.⁷ The same effect was observed here for O + C_2H_5OH at elevated temperatures. (2) The O-atom concentrations used in these measurements were very low and, in order to minimize any heterogeneous contribution, it was necessary to obtain data with a teflon coating on the tube that is usable only at low temperatures. Our results as shown in Figure 5 can be described as follows: (1) There is a strong dependence of the observed bimolecular rate constant, k_{obsd} , on the initial O-atom concentration even for such low concentrations as $2 \times 10^{10} \le [O]_0$ $< 2 \times 10^{11}$ atoms cm⁻³. (2) This dependence is less pronounced in the presence of O_2 , the observed rate constants being surprisingly smaller. (3) Both curves converge for $[O]_0 < 2 \times 10^{10}$ to a common value of approximately 5×10^{-14} cm³ molecule⁻¹ s⁻¹. In Reaction of $O(^{3}P)$ with Ethanol

TABLE I: Rate Constant Data for $O(^{3}P) + C_{2}H_{5}OH$ from the Discharge Flow-Resonance Fluorescence Experiment						
<i>T</i> /K	P _T /Torr	<i>v</i> /cm s ⁻¹	$[O]_0/atoms cm^{-3}$	$\frac{[C_2H_5OH]/10^{14}}{\text{molecules cm}^{-3}}$	K/s ⁻¹	
298 ± 0	1.748 ± 0.012	1227 ± 5	1.72×10^{10}	2.75 4.82	15.0 27.1	

				6.70	35.3
				8.39	44.6
				10.80	57.1
				12.72	67.4
	$k_1 = (5.20 \pm$	$\pm 0.07) \times 10^{-14} \text{ cm}^3 \text{ m}^3$	$\text{olecule}^{-1} \text{ s}^{-1}; \Delta K_{\text{w}} = 1.05$	$\pm 0.62 \text{ s}^{-1}$	
299 ± 0	2.004 ± 0.006	1391 ± 9	2.1×10^{10}	5.13	27.7
				6.69	38.9
				8.44	47.1
				11.34	59.5
				13.27	71.7
	$k_1 = (5.15)$	\pm 0.26) × 10 ⁻¹⁴ cm ³ r	nolecule ⁻¹ s ⁻¹ ; $\Delta K_{\rm w} = 2.8$	$\pm 2.4 \text{ s}^{-1}$	
338 ± 1	2.431 ± 0.008	1453 ± 13	3.9×10^{10}	2.84	36.9
				3.73	46.1
				6 60	74.8
				9.64	100.0
				12.8	132.8
				16.27	159.8
	$k_1 = (9.21)$	± 0.18) × 10 ⁻¹⁴ cm ³ r	nolecule ⁻¹ s ⁻¹ ; $\Delta K_w = 12$	$\pm 0.8 \mathrm{s}^{-1}$	
445 ± 5	2.529 ± 0.022	1878 ± 21	3.6×10^{10}	1.01	64.5
				2.12	117.0
				3.54	176.0
				5.34	238.4
				7.25	307.3
				8.66	373.0
	$k_1 = (3.91 :$	\pm 0.09) × 10 ⁻¹³ cm ³ m	olecule ⁻¹ s ⁻¹ ; $\Delta K_{\rm w} = 30.9$	$\pm 4.9 \text{ s}^{-1}$	
663 ± 4	2.547 ± 0.008	2674 ± 6	4.7×10^{10}	0.197	59.2
005 = 4				0.471	113.7
				1.04	229.9
				1.57	338.0
				1.57 1.93	338.0 399.8
	$k_1 = (1.99 :$	\pm 0.03) × 10 ⁻¹² cm ³ m	olecule ⁻¹ s ⁻¹ ; $\Delta K_w = 21.3$	1.57 1.93 $\pm 3.6 \text{ s}^{-1}$	338.0 399.8
706 ± 6	$k_1 = (1.99 = 1.936 \pm 0.010)$	\pm 0.03) × 10 ⁻¹² cm ³ m 3022 \pm 13	olecule ⁻¹ s ⁻¹ ; $\Delta K_w = 21.3$ 1.6 × 10 ¹¹	1.57 1.93 $\pm 3.6 \text{ s}^{-1}$ 0.117	338.0 399.8 54 3
706 ± 6	$k_1 = (1.99 \pm 1.936 \pm 0.010$	\pm 0.03) × 10 ⁻¹² cm ³ m 3022 ± 13	olecule ⁻¹ s ⁻¹ ; $\Delta K_w = 21.3$ 1.6 × 10 ¹¹	$\begin{array}{c} 1.57 \\ 1.93 \\ \pm 3.6 \ \mathrm{s}^{-1} \\ 0.117 \\ 0.283 \end{array}$	338.0 399.8 54.3 117 8
706 ± 6	$k_1 = (1.99 \pm 1.936 \pm 0.010$	\pm 0.03) × 10 ⁻¹² cm ³ m 3022 ± 13	olecule ⁻¹ s ⁻¹ ; $\Delta K_w = 21.3$ 1.6 × 10 ¹¹	$ \begin{array}{r} 1.57 \\ 1.93 \\ \pm 3.6 \ \mathrm{s}^{-1} \\ 0.117 \\ 0.283 \\ 0.532 \\ \end{array} $	338.0 399.8 54.3 117.8 189.9
706 ± 6	$k_1 = (1.99 \pm 1.936 \pm 0.010$	\pm 0.03) × 10 ⁻¹² cm ³ m 3022 ± 13	olecule ⁻¹ s ⁻¹ ; $\Delta K_w = 21.3$ 1.6 × 10 ¹¹	$ \begin{array}{r} 1.57 \\ 1.93 \\ \pm 3.6 \ \mathrm{s}^{-1} \\ 0.117 \\ 0.283 \\ 0.532 \\ 0.77 \\ \end{array} $	338.0 399.8 54.3 117.8 189.9 247.0

 $k_1 = (2.78 \pm 0.13) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}; \Delta K_w = 21.3 \pm 3.6 \text{ s}^{-1}$

order to account for this behavior we propose the mechanism given in Table III. In this simple model, reaction 1 is assumed to produce CH₃CHOH radicals exclusively, which seems justified by the measurements of Washida.⁶ The same simplification is assumed to hold for reaction 2. The fast reaction of CH₃CHOH radicals with O_2 , reaction 4, has been measured,¹⁷ and a fast reaction of CH₃CHOH with O atoms, reaction 3, was also assumed in this model. Provided that reaction 3 can compete sufficiently with reaction 1, reaction 3 establishes a chain together with reaction 2. Addition of O_2 partly intercepts this chain by reaction 4. With the exception of k_3 , all important rate coefficients are known (the recombination reactions are fortunately less important). For the determination of k_3 , strictly all individual O-atom decay profiles should be compared with simulated ones. This would not only be very cumbersome but also leaves the question open of how to account for a change of wall conditions occurring in the course of the reaction. Since a change in the wall seems to be inevitable in the $C_2H_5OH + O$ system, all attempts were made to eliminate its contribution by applying the usual first-order treatment even in the regime where subsequent reactions interfere, i.e., by determining the observed bimolecular rate coefficients as slopes in the plots of first-order rate coefficients

vs. ethanol concentration, K_c vs. [C₂H₅OH]. Such a treatment, of course, requires that the O-atom decay curves do not deviate too much from an exponential. Therefore, the upper limit for the initial O-atom concentration had to be 2×10^{11} atom cm⁻³. Even then the measured as well as the simulated K_c vs. [C₂H₅OH] curves were convex because the relative contribution of subsequent reactions decreases for high ethanol concentrations. Figure 6 shows a few simulated examples. Approximation of such a curve by a straight line would result in a positive intercept which is caused by the subsequent homogeneous reactions. In the case of a measured curve, therefore, the intercept is composed of a heterogeneous and a homogeneous contribution. However, the latter is very small if slopes are taken for comparison that refer only to "initial" portions of the K_c vs. [C₂H₅OH] plots. The measured as well as the calculated k^{app} values of Figure 5, therefore, refer to a range $0 < [C_2H_5OH] < 4 \times 10^{14}$ molecule cm^{-3} in the corresponding K_c vs. [C₂H₅OH] plots. Best fit for the measured k^{app} without additional O_2 (upper branch in Figure 5) was achieved for $k_3 = 1.7 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹. It is estimated that this value for k_3 is accurate only to about a factor of two. It should be mentioned that the upper branch in Figure 5 does not refer to the total absence of O_2 . Instead, O_2 surviving the discharge has been accounted for.

Discussion

Rate Constant Measurements. The problem described in the

⁽¹⁶⁾ Meier, U.; Grotheer, H.-H.; Riekert, G.; Just, Th. Chem. Phys. Lett. **1985**, 115, 221.

⁽¹⁷⁾ Riekert, G.; Grotheer, H.-H.; Meier, U.; Just, Th. to be submitted for publication.

TABLE II: Rate Constant Data for O	(³ P) +	C ₂ H ₅ OH from the Flas	h Photolysis-Resonance]	Fluorescence Experiment
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 A. O ₂ Source								
 T/K	C ₂ H ₅ OH/mTorr	O ₂ /Torr	total press./Torr	flash energy/J	K/s^{-1}	k_1/cm^3 molecule ⁻¹ s ⁻¹		
297 ± 0	220.4	0.48	100	90	383 ± 10	$(4.94 \pm 0.18) \times 10^{-14}$		
	220.4	0.48	100	46	380 ± 6	$(4.90 \times 0.13) \times 10^{-14}$		
		0.50	100	32-86	30 ± 3			
	44.87	1.01	100	29	127 ± 3	$(5.45 \pm 0.48) \times 10^{-14}$		
	44.87	1.01	100	60	135 ± 2	$(6.00 \pm 0.41) \times 10^{-14}$		
		1.00	100	32-69	48 ± 4			
		$k_1 =$	$(5.32 \pm 0.52) \times 10^{-5}$	¹⁴ cm ³ molecule ⁻¹	s ⁻¹			
383 ± 2	31.99	0.144	100	86	151 ± 23	$(1.86 \pm 0.34) \times 10^{-13}$		
	31.99	0.144	100	86	137 ± 19	$(1.69 \pm 0.23) \times 10^{-13}$		
	31.99	0.144	100	57	157 ± 21	$(1.93 \pm 0.26) \times 10^{-13}$		
		0.152	100	32-86	12 ± 5			
	31.99	1.03	100	60	174 ± 12	$(2.16 \pm 0.15) \times 10^{-13}$		
	31.99	1.03	100	32	174 ± 19	$(2.16 \pm 0.23) \times 10^{-13}$		
	31.99	1.03	100	69	177 ± 11	$(2.19 \pm 0.14) \times 10^{-13}$		
	31.99	1.03	100	66	178 ± 12	$(2.21 \pm 0.15) \times 10^{-13}$		
		1.00	100	32-94	28 ± 4			
		$k_1 =$	$(2.03 \pm 0.20) \times 10^{-5}$	¹³ cm ³ molecule ⁻¹	s ⁻¹			
544 ± 2	44.87	1.01	100	36	800 ± 33	$(9.72 \pm 0.44) \times 10^{-13}$		
••••=	44.87	1.01	100	69	816 ± 13	$(9.92 \pm 0.19) \times 10^{-13}$		
	44.87	1.01	100	66	744 ± 90	$(9.02 \pm 1.16) \times 10^{-13}$		
	44.87	1.01	100	66	776 ± 19	$(9.42 \pm 0.26) \times 10^{-13}$		
		1.00	100	32-86	26 ± 2	(
		$k_1 =$	$(9.52 \pm 0.39) \times 10^{-1}$	¹³ cm ³ molecule ⁻¹	s ⁻¹			
766 ± 3	5.5	1.06	100	63	300 ± 11	$(3.71 \pm 0.20) \times 10^{-12}$		
	5.5	1.06	100	63	274 ± 14	$(3.33 \pm 0.25) \times 10^{-12}$		
	5.5	1.06	100	60	266 ± 7	$(3.22 \pm 0.14) \times 10^{-12}$		
	5.5	1.06	100	60	276 ± 6	$(3.36 \pm 0.13) \times 10^{-12}$		
	5.5	1.06	100	60	267 ± 5	$(3.23 \pm 0.12) \times 10^{-12}$		
	5.5	1.06	100	32	278 ± 5	$(3.39 \pm 0.12) \times 10^{-12}$		
		1.00	100	32-94	43 ± 3	· ,		
		$k_1 =$	$(3.37 \pm 0.18) \times 10^{-1}$	¹² cm ³ molecule ⁻¹	s ⁻¹			
B. NO Source								
 T/K	C ₂ H ₅ OH/mTorr	NO/Torr	total press./Torr	flash energy/J	K/s ⁻¹	k_1/cm^3 molecule ⁻¹ s ⁻¹		
 514 ± 2	12.47	0.253	50	57	332 ± 37	$(7.12 \bullet 1.79) \times 10^{-13}$		
	12.47	0.253	50	86	311 ± 12	$(6.22 \pm 0.72) \times 10^{-13}$		
	12.47	0.253	50	38	316 ± 21	$(6.44 \pm 1.11) \times 10^{-13}$		
	12.47	0.253	50	76	324 ± 29	$(6.78 \pm 1.45) \times 10^{-13}$		
		0.250	50	25-94	165 ± 5			
$k_1 = (6.64 \pm 0.39) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$								
886 ± 2	12.47	0.253	50	38	932 ± 28	$(6.04 \pm 0.32) \times 10^{-12}$		
	12.47	0.253	50	90	926 ± 27	$(6.00 \pm 0.29) \times 10^{-12}$		
	12.47	0.253	50	60	944 ± 10	$(6.13 \pm 0.19) \times 10^{-12}$		
		0.250	50	43-90	111 ± 16	· · · · · · · · · · · · · · · · · · ·		
		$k_1 =$	$(6.06 \pm 0.27) \times 10^{-1}$	¹² cm ³ molecule ⁻¹	s ⁻¹			

previous section is but one example of the general problem: slow primary reaction leading to very reactive products. An excellent discussion of this problem was given for the $O(^{3}P) + H_{2}$ reaction studied by Presser and Gordon.²⁰ In general, this problem can be overcome by making measurements at small residence times and/or at large stoichiometry between the reactants. These requirements were readily met in the flash photolysis experiments. In the flow reactor, mixing set the lower limit for the reaction time. Background and particularly wall effects determined the lowest O-atom concentration while the highest ethanol flows were limited by its vapor pressure at ambient temperature. Hence, in the flow tube work, it was necessary to use O_2 as a scavenger for CH₃CHOH radicals together with quite low initial O-atom concentrations of 2×10^{10} to 5×10^{10} atoms cm⁻³. At significantly higher O-atom concentrations, k_1 could not be deduced directly from the observed O-atom decays as shown in Figure 5, and modeling was required. Since the studies of Roscoe³ and Faubel⁵ were perturbed by secondary reactions, it is not reasonable to compare their data with the present results. In contrast, this

argument does not hold under the conditions ($[O]_0 = (2.8-3.4)$) $\times 10^{14}$ atoms cm⁻³, [C₂H₅OH]₀ = (3.9-7.8) $\times 10^{12}$ molecules cm⁻³) of Washida,⁶ where any disturbing radicals like CH₃CHOH, OH, or HO₂ should have been quenched by the excess of oxygen atoms, thus leaving the C_2H_5OH decays undisturbed. Perhaps the large C₂H₅OH decays of Washida are caused by O₂($^{1}\Delta$), which is always generated from an O_2 discharge.²¹ It is not likely for this potential problem to exist in the present work because the oxygen concentration was four orders of magnitude lower. In confirmation of this, it has been found, in the related CH₃OH + O system under similar conditions,⁷ that the O-atom decays were independent of the particular O-atom source used.

For the high $k_1(298)$ result of Kato and Cvetanovic,¹ it is possible to provide only a qualitative explanation also. They used the continuous, mercury-sensitized photolysis of N₂O as a source of $O({}^{3}P)$ atoms together with very high ethanol concentrations of $\sim 1 \times 10^{18}$ molecule cm⁻³. From their light intensities and our k_1 we estimate a steady-state concentration of $[O]_{ss} = (1-2) \times$ 10⁹ atoms cm⁻³. Under their conditions, Kato and Cvetanovic assumed the mechanism:

$$C_2H_5OH + O \rightarrow CH_3CHOH + OH \tag{1}$$

$$C_2H_5OH + OH \rightarrow CH_3CHOH + H_2O$$
 (2)

(21) Jones, I. T. N.; Bayes, K. D. J. Chem. Phys. 1973, 59, 3119.

⁽¹⁸⁾ Sridheran, U. C.; Qiu, L. X.; Kaufman, F. J. Phys. Chem. 1982, 86, 4569.

⁽¹⁹⁾ As recommended by J. Warnatz in Gardiner, Jr., W. C., Ed. Com-(20) Presser, N.; Gordon, R. J. J. Chem. Phys. 1985, 82, 1291.



Figure 4. Arrhenius plot of bimolecular rate constant for reaction 1: O, this work, DF-RF; ●, this work, FP-RF; ⊕, Washida;⁶ □, Kato and Cvetanovic;¹ **2**, Ayub and Roscoe.⁴



Figure 5. Apparent bimolecular rate coefficients for reaction 1 as a function of initial O-atom concentration. T = 298 K, and teflon coated tube. Open circles are for low $[O_2]$ ($\leq 10^{12}$ molecules/cm³) and full circles are for $[O_2] \ge 10^{14}$ molecules/cm³. The solid curves are the results of the computer simulations using the mechanism of Table III with $k_3 = 1.7 \times 10^{-10} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$ (see text).

 $2CH_3CHOH \rightarrow CH_3CHO + C_2H_5OH$ (8)

$$2CH_3CHOH \rightarrow (CH_3CHOH)_2$$
 (9)

In the absence of 1-butene (see below) this mechanism seems to apply. Under the assumption of $k_{(8+9)} \simeq 1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ s⁻¹, we get $[CH_3CHOH]_{ss} = 2 \times 10^{12}$ molecules cm⁻³. Thus $k_3[CH_3CHOH]_{ss}/(k_1[C_2H_5OH]) \simeq 10^{-2}$, i.e., O-atom consumption by reaction 3 indeed plays no significant role under the conditions of Kato and Cvetanovic. k_1 was determined relative to the known rate coefficient of $O + 1-C_4H_8$ by adding 1-butene to the ethanol in a 1:10 ratio. However, [O]_{ss} was not monitored, but rather the acetaldehyde yields were measured in the presence



Figure 6. First-order rate constants, K, for reaction 1 vs. [C₂H₅OH]. Values for K were obtained from modeled O-atom decays (a) in the absence and (b) in the presence of added O_2 ($\geq 10^{14}$ molecules/cm³). The initial O-atom concentrations are as follows: solid lines, 5×10^{11} atoms/cm³; dashed lines, 1.5×10^{11} atoms/cm³; dotted lines, 5×10^{10} atoms/cm³. A value of $k_3 = 2 \times 10^{-10}$ cm³ molecules⁻¹ s⁻¹ was used (see text).

and absence of 1-butene under the assumption that the mechanism outlined above would remain undisturbed.

This is not the case with respect to the consumption of OH radicals. At room temperature the rate coefficient for OH + $1-C_4H_8$ is 3.3×10^{-11} cm³ molecule⁻¹ s⁻¹,¹⁹ i.e., roughly 20 times k_2 . Thus, under the conditions of Kato and Cvetanovic¹ in the absence of 1-C₄H₈, all OH radicals would produce CH₃CHOH by reaction with ethanol, but only one-third would react this way in the presence of $1-C_4H_8$. While the effect of this reaction goes in the wrong direction, it shows where problems might enter. Consider, for example

$$CH_3CHOH + 1-C_4H_8 \rightarrow CH_3CHO + C_4H_9$$

which is slightly exothermic by $\Delta H_r = -48.5$ according to the heats of formation (in kJ/mol at 298 K):

$$\Delta H_{f}(CH_{3}CHOH) = -63.7 \text{ (ref 22)}$$

$$\Delta H_{f}(1-C_{4}H_{8}) = 0.4 \text{ (ref 22)}$$

$$\Delta H_{f}(CH_{3}CHO) = -166.2 \text{ (ref 23)}$$

$$\Delta H_{f}(S-C_{4}H_{9}) = 54.4 \text{ (ref 22)}$$

In the presence of $1-C_4H_8$, the latter reaction might lead to higher CH₃CHO yields than by reactions 8 and 9 alone. Hence, an erroneously high value for k_1 could have been derived. In order to account for the effects of undesired side reactions, Kato and Cvetanovic always extrapolated to zero time. Reactions of the kind described, however, could not have been observed by this method, since $[C_2H_5OH]$ and $[1-C_4H_8]$ remain virtually constant, while radicals like CH₃CHOH and OH are nearly instantaneously in their steady states.

Two additional remarks on k_1 should be made. The k_1 expression quoted by Westbrook and Dryer²⁴ reproduces the present result at about 1000 K only fortuitously. It was taken from an earlier study on ethanol ignition,²⁵ in which the Arrhenius parameters of Roscoe^{3,4} were used, but with the A factor erroneously one order of magnitude too high.

We obtained a value of k_1 by the use of linear free energy correlations²⁶ which, for a number of compounds, correlate the

⁽²²⁾ McMillan, D. F.; Golden, D. M. Annu. Rev. Phys. Chem. 1982, 33, 493.

⁽²³⁾ Baulch, D. L.; Cox, R. A.; Hampson, Jr., R. F.; Kerr, J. A.; Troe, J.; Watson, R. T. J. Phys. Chem. Ref. Data 1984, 13, 1259.
 (24) Westbrook, C. K.; Dryer, F. L. Prog. Energy Combust. Sci. 1984, 10,

^{1.}

⁽²⁵⁾ Natarajan, K.; Bhaskaran, K. A. Shock Tube, Proc. Int. Symp. 13th, 1981 1982, 834-842.

TABLE III: Reaction Mechanism

no.	reaction	rate constant/cm ³ molecule ⁻¹ s ⁻¹	ref
1	$O + C_3H_4OH \rightarrow OH + CH_3CHOH$	5×10^{-14}	this study
2	$OH + C_3H_3OH \rightarrow H_2O + CH_3CHOH$	1.75×10^{-12}	16
3	O + CH ₃ CHOH → OH + CH ₃ CHO	2×10^{-10}	derived ^b
4	$O_2 + CH_3 CHOH \rightarrow HO_2 + CH_3 CHO$	2×10^{-11}	17
5	$O + HO_2 \rightarrow OH + O_2$	5.5×10^{-11}	18
6	$CH_3CHOH \rightarrow products$	$50 \times s^{-1 a}$	estimated
7	$OH + HO_2 \rightarrow H_2O + O_2$	3×10^{-11}	19

^a First-order rate constant. ^b Derived from model simulations in this study.

abstraction reaction rates by O atoms and OH radicals, respectively, within a factor of about 2. In the case of CH₃OH + OH^{27,28} and CH₃OH + O^{7,8} these correlations are remarkably well fulfilled. "Prediction" by LFE correlations of $k_1(298)$ from the known rate coefficient for ethanol + OH¹⁶ yields k_1 (pred) = 2 × 10⁻¹⁴ cm³ molecule⁻¹ s⁻¹ which is lower than the present experimental value for k_1 by somewhat more than the stated uncertainty of the method. Thus this result clearly suggests, by the analogy to the CH₃OH reaction, that the "low" k_1 value of the present work is to be favored over those of the earlier studies.

The $CH_3CHOH + O$ Reaction. Under the conditions of high radical concentrations (i.e., $[O]_0 \simeq 10^{13}$ atoms cm⁻³, CH₃OH excess), addition of O_2 led to an increase of the observed (overall) reaction rate in the CH₃OH + O system.²⁹ Under the same conditions the opposite occurred in the $C_2H_5OH + O$ system.³ Conversely, under low radical concentrations ($\sim 10^{11}$ cm⁻³) addition of O_2 had virtually no effect on the CH₃OH + O system,⁷ while it strongly affected our observed rate constants for C₂H₅OH + O. This led us to conclude that the $CH_2OH + O$ reaction is slow and that CH₃CHOH radicals are more reactive toward O atoms than HO_2 radicals are. Using the simple model in Table III, we obtained a value of $k_3 = 1.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ A rate coefficient of that order has been suggested by Washida.⁶ He actually measured a value of $k_4/k_3 = 0.14 \pm 0.04$ for the competition of O₂ molecules and O atoms for CH₃CHOH radicals. This ratio together with a direct measurement of $k_4 = 3 \times 10^{-11}$ cm³ molecule⁻¹ s^{-1 17} gives $k_3 = 2 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ in good agreement with the value derived from our model. It is this fast secondary reaction that makes the k_1 measurement so difficult under conditions of C₂H₅OH excess.

Branching of the $O({}^{3}P) + C_{2}H_{5}OH$ Reaction. The rate data for reaction 1 obtained in this study, as summarized in Figure 4, clearly exhibit non-Arrhenius behavior. Among several possible explanations, this result might be due to the effect of branching ratios for reaction 1 that display dissimilar temperature coefficients. This idea follows from the thermochemical data for the three possible H-abstraction channels for reaction 1:

 $O(^{3}P) + C_{2}H_{5}OH \rightarrow CH_{3}CHOH + OH$ $\Delta H_{r} = -38.6 \text{ kJ/mol} (1a)$ $\rightarrow CH_{2}CH_{2}OH + OH \qquad \Delta H_{r} = -30.1 \text{ kJ/mol} (1b)$ $\rightarrow C_{2}H_{5}O + OH \qquad \Delta H_{r} = 7.9 \text{ kJ/mol} (1c)$ At ambient temperatures reaction 1a is reported to be the dominant channel from studies of Washida,⁶ and Kato and Cvetanovic,¹ although calibrations were not performed. At higher temperatures, the existing experimental results lead to an incomplete and conflicting picture for branching in reaction 1. In this regard, a report³⁰ has been prepared in which we speculate, in some detail, on the branching ratios for reaction 1 and on the temperature dependence of the rate constants for the H-abstraction channels. The conclusion of this speculative report is that the temperature dependence of the present result for $k_1(T)$ might be described by a double exponential fit derived from rate expressions that presumably represent k_{1a+1b} and k_{1c} . The derived, double exponential expression is

$$k_1(T) = 3.2 \times 10^{-11} \exp(-1960/RT) + 8.0 \times 10^{-11} \exp(-3450/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

This expression is presented here without further substantiation. Although it was admittedly derived by making a number of assumptions, it could be of value in making comparisons with kinetic results (both previous and future) that lie outside the present temperature range. Undoubtedly, direct experiments on the branching in reaction 1 are certainly needed to clarify this question.

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Registry No. Atomic oxygen, 17778-80-2; ethanol, 64-17-5; oxygen, 7782-44-7; hydrogen, 1333-74-0.

 ⁽²⁶⁾ Gaffney, J. S.; Levine, S. Z. Int. J. Chem. Kinet. 1979, 11, 1197.
 (27) Hägele, J.; Lorenz, K.; Rhäsa, D.; Zellner, R. Ber. Bunsenges. Phys. Chem. 1983, 87, 1023.

⁽²⁸⁾ Meier, U.; Grotheer, H.-H.; Just, Th. Chem. Phys. Lett. 1984, 106, 97.

⁽²⁹⁾ Grotheer, H.-H.; Riekert, G.; Meier, U.; Just, Th. Ber. Bunsenges. Phys. Chem. 1985, 89, 187.

⁽³⁰⁾ Grotheer, H.-H.; Nesbitt, F. L.; Klemm, R. B. BNL Informal Report No. 37971, 1986; available from the authors on request.