The reaction of O(³P) atoms with ethane: An HTP kinetics study from 300 to 1270 K

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Rate coefficients for the O + C₂H₆ reaction have been measured using the high-temperature photochemistry (HTP) technique. Strong non-Arrhenius behavior is observed. The data are well fitted by the empirical expression $k(T) = 1.9 \times 10^{-31} T^{6.5} \exp(-138 \text{ K}/T)$ cm³ molecule⁻¹ s⁻¹. Confidence limits are discussed in the text. The results are consistent with calculations based on transition state theory and tunneling through an Eckart barrier.

I. INTRODUCTION

Non-Arrhenius behavior has frequently been observed in radical-molecule reactions studied over wide temperature ranges. However, the type of behavior and degree to which different causes contribute varies. Here, in the third of a series of studies of the reactions of O(³P) atoms with C₂ hydrocarbons^{1,2} we report kinetic measurements on the reaction

which is 4.3 kcal mol⁻¹ exothermic at 298 K.³

This reaction is thought to play a significant role in some fuel-lean combustion systems.⁴ Reliable evaluation of the role of reaction (1) in hydrocarbon oxidation depends on the availability of direct measurements over an extended temperature range. Previous low-temperature studies of this reaction⁵⁻⁹ show no deviation from Arrhenius behavior in the 298–650 K temperature range. More recent studies over the 595–1030⁴ and 416–1048 K¹⁰ temperature regimes also show no such deviation. However, a combination of the low- and high-temperature data suggests strong non-Arrhenius behavior. The present study was undertaken to obtain reliable kinetic data over a wide temperature range, using a single apparatus, to determine whether this indeed occurs. The high-temperature photochemistry (HTP) technique^{1,11} is used. Earlier experimental studies of this reaction over appreciable temperature ranges were all made by flow tube techniques. The present work thus allows a comparison of techniques in the regions of experimental overlap. Since the present study covers the widest temperature range over which experimental data have been obtained to date, it is also of interest for comparison to a recent theoretical prediction.¹²

II. TECHNIQUE

The basic principles and details of construction of the HTP reactor used have been described in detail previously^{1,11} and are only summarized here. Important features of this reactor include an alumina reaction tube, SiC resistance heating elements, and a movable cooled reactant inlet. The latter minimizes homogeneous and heterogeneous decomposition effects by allowing for short residence times for thermally unstable gases.

C₂H₆, along with the photolyte (CO₂ or O₂), is injected into the reactor through the cooled inlet, to mix with the

heated bath gas Ar. In this pseudostatic real time method, O atoms are generated by flash photolysis. Subsequent decrease in [O] through reaction (1) and diffusion is monitored by atomic resonance fluorescence with pulse counting and signal averaging. A 15 cm focal length CaF₂ plano-convex lens is attached to the resonance lamp to focus the exciting radiation and filter out the Lyman- α line. An EMI G-26E314LF photomultiplier tube (PMT) is used to detect the fluorescence. The PMT is connected to a Nicolet LAS 12/70 multichannel scaler via an EG&G PAR 1121-A amplifier discriminator.

A Pt/Rh thermocouple, with two radiation shields, is used to measure reaction zone temperatures. Flow and pressure measurements are made with Teledyne-Hastings digital flow meters and an MKS baratron, respectively. The resonance lamp operates on He(99.999%) supplied by Linde. The reactor gases used are Ar from the liquid (99.998%, U.H.P.), CO₂ (99.99%, precision aquarator), and O₂ (99.6%, zero grade), all from Linde. Ethane was obtained from Scientific Gas Products (99.98%, research grade) and Matheson (99.95%, research grade). 1.91% ethane (99.95%, research grade) in Ar (99.998%, prepurified) was supplied by Matheson.

Pseudo-first-order conditions, [C₂H₆] $\gg$ [O], apply in the HTP reactor. The pseudo-first-order rate coefficient k_{ps1} is determined from the relation

$$I_t = I_{t=0} \exp(-k_{\text{ps1}} t) + B \quad (2)$$

I_t is the fluorescence intensity at time t and B a background level, mostly accounted for by scattered light from the resonance lamp. Here,

$$k_{\text{ps1}} = k_1[\text{C}_2\text{H}_6] + k_D \quad (3)$$

k_D accounts for O-atom loss, essentially by diffusion.

Typically five to seven k_{ps1} values, obtained as a function of [C₂H₆] under the same general (P, T , etc.) conditions, are used to determine $k_1 \pm \sigma_{k_1}$, Table I. The data reduction and error analysis procedures for determining k_{ps1} , k_1 , and fitted expressions for $k_1(T)$ have been described in detail previously.^{1,11}

III. RESULTS AND DISCUSSION

Table I summarizes the 46 measurements of k_1 made from about 300 to 1270 K. Here, [M] denotes total concen-

TABLE I. Summary of rate coefficient measurements on $O + C_2H_6$.

T (K)	P (Torr)	$[M]$ (10^{18} cm^{-3})	$[C_2H_6]$ (10^{13} cm^{-3})	[Photolyte] (10^{15} cm^{-3})	$\bar{v}$ (cm s^{-1})	l (cm)	F (J)	$k \pm \sigma_k$ ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$)
297	267	8.67	(446–1070) ^c	4.46 ^a	6	22.8	32 ^s	1.28 ± 0.31 (–15)
297	144	4.69	(176–837) ^c	11.0 ^a	9	22.8	32 ^s	1.08 ± 0.12 (–15)
298	160	5.17	(243–881) ^d	9.52 ^a	9	22.8	37 ^s	1.35 ± 0.20 (–15)
300	184	5.88	(212–921) ^c	11.0 ^a	7	22.8	37 ^s	1.84 ± 0.30 (–15)
321	209	6.30	(285–869) ^c	18.5 ^a	8	22.8	32 ^s	1.54 ± 0.20 (–15)
325	209	6.19	(163–609) ^c	9.27 ^a	8	22.8	32 ^s	1.49 ± 0.34 (–15)
347	186	5.18	(115–479) ^c	7.40 ^a	8	22.8	43 ^s	3.42 ± 0.64 (–15)
347	186	5.18	(115–479) ^c	7.40 ^a	8	22.8	19 ^s	3.76 ± 0.54 (–15)
358	437	11.7	(207–1100) ^c	8.90 ^a	3	22.8	37 ^s	2.77 ± 0.95 (–15)
369	97	2.54	(63–316) ^c	4.58 ^a	15	22.8	43 ^s	5.10 ± 0.42 (–15)
380	210	5.34	(53–204) ^c	12.9 ^a	9	22.8	43 ^s	6.06 ± 0.67 (–15)
380	210	5.34	(53–204) ^c	12.9 ^a	9	22.8	12 ^s	8.20 ± 1.60 (–15)
423	209	4.76	(32–148) ^c	12.3 ^a	11	22.8	43 ^s	1.51 ± 0.10 (–14)
423	209	4.76	(32–148) ^c	12.3 ^a	11	22.8	19 ^s	1.36 ± 0.14 (–14)
483	167	3.34	(19–183) ^c	4.94 ^a	15	22.8	48 ^s	4.25 ± 0.29 (–14)
483	167	3.34	(24–72) ^c	4.94 ^a	15	2.28	37 ^s	3.02 ± 0.90 (–14)
519	483	9.00	(69–280) ^c	14.6 ^a	6	13.2	27 ^m	3.14 ± 0.15 (–14)
520	455	8.41	(79–260) ^c	20.8 ^a	5	13.2	27 ^m	3.72 ± 0.16 (–14)
547	241	4.32	(11–139) ^c	7.88 ^a	13	13.2	15 ^m	6.74 ± 1.41 (–14)
568	621	1.05	(69–263) ^c	19.0 ^a	3	13.2	19 ^m	1.20 ± 0.09 (–13)
615	321	5.06	(1.6–26.6) ^c	121 ^b	9	8.2	19 ^m	1.68 ± 0.08 (–13)
622	320	4.98	(4.0–24.0) ^c	122 ^b	9	13.2	19 ^m	2.42 ± 0.13 (–13)
624	159	2.51	(15–60) ^c	51 ^b	21	22.8	48 ^s	2.34 ± 0.12 (–13)
641	218	3.30	(20–141) ^c	9.61 ^a	9	13.2	19 ^m	2.51 ± 0.10 (–13)
716	393	5.30	(23–140) ^c	9.04 ^a	10	13.2	19 ^m	4.28 ± 0.04 (–13)
758	325	4.16	(4.0–21.4) ^c	86 ^b	11	8.2	19 ^m	6.37 ± 0.40 (–13)
831	321	3.74	(2.4–150) ^c	81 ^b	12	13.2	19 ^m	1.51 ± 0.20 (–12)
887	326	3.55	(5.9–13.1) ^c	74 ^b	13	8.2	27 ^m	1.96 ± 0.03 (–12)
1002	320	3.08	(1.8–7.7) ^c	63.7 ^b	14	8.2	27 ^m	3.98 ± 0.30 (–12)
1012	321	3.08	(1.3–7.1) ^c	63.7 ^b	14	8.2	7 ^m	3.91 ± 0.09 (–12)
1052	553	5.08	(1.6–7.7) ^c	57.7 ^b	10	6	32 ^m	3.67 ± 0.35 (–12)
1053	254	2.33	(0.95–5.2) ^c	50.0 ^b	22	6	32 ^m	5.10 ± 0.33 (–12)
1058	270	2.47	(0.80–9.3) ^c	52.8 ^b	12	6	32 ^m	4.68 ± 0.10 (–12)
1064	309	2.83	(0.10–0.29) ^c	42.2 ^b	21	8.2	37 ^m	5.38 ± 0.10 (–12)
1064	312	2.83	(0.11–0.40) ^c	40.6 ^b	21	8.2	19 ^m	3.90 ± 0.22 (–12)
1064	312	2.83	(0.11–0.40) ^c	40.6 ^b	21	8.2	37 ^m	3.54 ± 0.30 (–12)
1124	173	1.51	(0.55–1.9) ^c	25.6 ^b	29	6	27 ^m	9.52 ± 0.20 (–12)
1125	248	2.13	(0.46–5.10) ^c	45.8 ^b	24	4	32 ^m	7.98 ± 0.30 (–12)
1128	276	2.36	(0.46–3.5) ^c	23.6 ^b	13	4	22 ^m	8.19 ± 0.11 (–12)
1145	307	2.58	(0.30–2.3) ^c	36.6 ^b	23	6	32 ^m	9.04 ± 0.36 (–12)
1161	310	2.58	(0.67–2.4) ^c	37.5 ^b	23	8.2	32 ^m	1.18 ± 0.06 (–11)
1177	267	2.17	(0.51–1.6) ^c	35.0 ^b	22	6	37 ^m	1.21 ± 0.05 (–11)
1224	270	2.12	(0.37–1.3) ^c	22.2 ^b	45	4	37 ^m	2.33 ± 0.10 (–11)
1230	254	2.10	(0.35–1.3) ^c	41.0 ^b	25	4	37 ^m	1.63 ± 0.12 (–11)
1232	231	1.82	(0.70–1.7) ^c	35.2 ^b	19	4	37 ^m	2.67 ± 0.07 (–11)
1267	269	2.05	(0.40–1.2) ^c	31.8 ^b	24	6	37 ^m	2.42 ± 0.20 (–11)

^a O_2 used as photolyte.^b CO_2 used as photolyte.^c Pure ethane, Matheson.^d Pure ethane, Scientific gas.^e 1.91% ethane in argon, Matheson.^s Sapphire window between flash lamp and reactor.^m MgF_2 window between flash lamp and reactor.

tration, F represents the energy dissipated in the flash lamp per flash, $\bar{v}$ the average gas velocity, and l the distance between the tip of the cooled inlet and the center of the observed reaction zone.

The experiments were performed over a wide range of $[M]$ [(1.5 to 11.7) $\times 10^{18} \text{ cm}^{-3}$] and $\bar{v}$ (3 to 45 cm s^{-1}) and five values of l . The data reveal no consistent variation of k_1 with $[M]$. The results are also seen to be independent of $l\bar{v}^{-1}$, the mean-residence time, indicating there has been no

significant pyrolysis of C_2H_6 and that thermal equilibrium and mixing between the bath gas and reactants has been achieved.¹³ O_2 has been used as photolyte from 297 to 716 K and CO_2 as photolyte from 615 to 1267 K. No significant difference in k_1 values with photolyte is present in the overlap region. Because of the slow reaction rate at low temperatures, a possible source of error which has to be considered is impurities in the ethane, particularly ethylene. The Matheson 99.95% C_2H_6 contained 310 ppm ethylene as the only

significant impurity, according to the manufacturers analysis. Since the $O + C_2H_4$ reaction has a considerably larger rate coefficient, as determined with the present HTP apparatus,¹ the k_1 values between 297 and 483 K obtained using that cylinder, have been reduced by its contribution. This is a minor correction which amounts to 14% at 297 K and less at higher temperatures. With this correction, there are no discernible differences between the results obtained with the various cylinders and thus the influence of impurities is negligible. As a further check, the C_2H_6 was passed through a dry ice trap in some experiments, again yielding results consistent with the other runs.

Results obtained with a sapphire window between the flash lamp and the reactor are independent of F , varied from 7 to 48 J, cf. Table I. However, measurements made with a MgF_2 window are independent of F only over the 500–1270 K temperature range. At lower temperatures the measured k_1 values decreased with F and only at the lowest flash energies tended toward the values obtained with the sapphire window. This observation may be attributed to the slow reaction rate at low temperatures and consequent large $[C_2H_6]$ needed to make k_1 measurements. This large $[C_2H_6]$ leads to significant $[C_2H_4]$, the principal photolysis product of C_2H_6 .^{14,15} The relatively fast O/C_2H_4 reaction thus competes with the O/C_2H_6 reaction. With a sapphire window, which has a nominal 145 nm cutoff,^{14,16} as compared to the 115 nm cutoff^{16,17} of MgF_2 , the C_2H_6 photolysis is essentially negligible. Above 500 K, experiments per-

formed with either window led to indistinguishable results, cf. Table I.

The k_1 data are plotted in Fig. 1. A strongly curved plot is obtained. A purely empirical fit of the form $A T^n \times \exp(-E/T)$ to these data gives

$$k_1(T) = 1.90 \times 10^{-31} (T/K)^{6.5} \times \exp(-138 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (4)$$

with variances and covariances $\sigma_A^2 = 4.27 \times 10^{-61}$, $\sigma_{An} = -3.00 \times 10^{-31}$, $\sigma_n^2 = 2.11 \times 10^{-1}$, $\sigma_{AE} = 1.77 \times 10^{-28}$, $\sigma_E^2 = 7.53 \times 10^4$, $\sigma_{nE} = -1.24 \times 10^2$.

Since the parameters are dependent, we need to take into account both the variances associated with each parameter and the covariances associated with the different pairs of parameters to calculate confidence intervals¹⁸ for the $k_1(T)$ expression. This leads to a confidence interval of approximately 7% at the 1σ level. From previous experience with rate coefficients determined by different workers for the $O + C_2H_4$ ¹ and $O + C_2H_2$ ² reactions, we allow for possible systematic errors of about 25%. This leads to confidence intervals of about 27%, at the 1σ level, over the 300–1270 K temperature range.

A comparison of the present data to other important studies of reaction (1) is presented in Fig. 2. These include the flow reactor study of Caymax and Peeters⁴ over the 600–

FIG. 1. Summary of the HTP measurements of the $O + C_2H_6$ rate coefficient from 300 to 1270 K.

FIG. 2. Comparison of present k_1 values to some other major determinations of the temperature dependence of the $O + C_2H_6$ rate coefficient above 300 K. Literature curves from Tanzawa and Klemm (Ref. 10), Caymax and Peeters (Ref. 4), Herron and Huie (Ref. 9) (recommendation), and Papadopoulos, Ashmore, and Tyler (Ref. 8).

1030 K range and the experiments of Tanzawa and Klemm¹⁰ over the 415–1050 K temperature range. The latter work consists of flow reactor and flash photolysis-resonance fluorescence studies over the 450–1050 and 415–520 K temperature ranges, respectively. Also shown is the recommendation of Herron and Huie⁹ for the range 298–650 K, based on earlier work, and the study of Papadopoulos *et al.*⁸ over the 300–360 K range, all of which were made in flow reactors. Satisfactory agreement with the present work, in the respective regions of temperature overlap, is seen in every case.

In Fig. 3 the present data set as represented by Eq. (4) is compared to the analysis of Cohen and Westberg¹² using transition state theory (TST). Agreement between our data and their analysis is seen to be excellent at $T \gtrsim 400$ K. However, their study indicates significantly smaller k_1 values than evident from the present study and other experimental work at $T \lesssim 400$ K.^{8,9} They expressed k_1 as

$$k_1(T) = 1.66 \times 10^{-21} [10^{9.23} \exp\{\Delta S^\ddagger(T_1)/R\}]^{[(T-T_1)/T]} \times [k_1(T_1)/T_1^2]^{(T_1/T)} \times \exp(I_1 + I_2) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (5)$$

where

FIG. 3. Comparison of theoretical calculations with experimental data for $\text{O} + \text{C}_2\text{H}_6$. (—) Fit to experimental data of present study. (---) TST study of Cohen and Westberg (Ref. 12) (— · —) TST calculations incorporating quantum-mechanical tunneling through an Eckart barrier, see the text.

$$I_1 = (1/R) \int_{T_1}^T \Delta C_p^\ddagger \frac{dT}{T} = [\Delta S^\ddagger(T) - \Delta S^\ddagger(T_1)]/R, \\ I_2 = [-1/(RT)] \int_{T_1}^T \Delta C_p^\ddagger dT \\ = -\{[\Delta H^\ddagger(T) - \Delta H^\ddagger(T_1)]/(RT)\}.$$

This treatment takes small degrees of tunneling into account and is based on an estimated value of $k_1(T_1 = 298 \text{ K}) = 2.6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This value is a factor of 2 to 5 lower than all experimental data at room temperature.^{12,19} Though Eq. (4) represents a purely empirical fit to the present data set, the high value of n is consistent with tunneling being a significant source of curvature in the Arrhenius-type plot.²⁰ Rate coefficients for several other H-atom transfer reactions, at similarly low temperatures, have been shown to be consistent with TST calculations incorporating quantum-mechanical tunneling based on an Eckart potential.^{11,21,22} A similar correction is therefore applied here to the TST analysis of Cohen and Westberg.

$\Delta C_p^\ddagger(T)$ is determined using $C_p(T)$ data for O atoms²³ and information on vibrational frequencies and properties of internal rotors for the activated complex and C_2H_6 .^{12,24} Initial estimates of the barrier heights at 0 K are made using Eq. (4), heats of formation,^{3,25} and $\Delta C_p^\ddagger(T)$. The latter quantity is also used to estimate $\Delta S^\ddagger(T)$ from $\Delta S^\ddagger(298 \text{ K})$ given by Cohen and Westberg.¹² The "frequency" along the reaction coordinate w is taken to be $1600i \text{ cm}^{-1}$.²⁶ The barrier heights then determine initial estimates of the Eckart parameters²⁷ and hence $\Gamma^*(T)$, the tunneling factor. New estimates of barrier heights and $\Gamma^*(T)$ are subsequently made using Eq. (5) with $T_1 = 600 \text{ K}$ and $k_1(T_1) = k_1(T_1)_{\text{experimental}}/\Gamma^*(T_1)$. The procedure is repeated until convergence. Final calculations show the barrier heights in the forward and reverse directions to be 12 and 16.8 kcal/mol⁻¹ with $\Gamma^*(T)$ decreasing from approximately 27 at 300 K to 1.16 at 1300 K.

These calculations lead to

$$k_1(T) = 3.21 \times 10^{-26} T^{4.85} \times \exp(-1021 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}, \quad (6)$$

which is plotted in Fig. 3. As seen there, agreement with the fit to the experimental data as represented by Eq. (4) is excellent.

IV. CONCLUDING REMARKS

The $\text{O} + \text{C}_2\text{H}_6$ reaction shows pronounced curvature in its Arrhenius-type plot. This is not evident from the earlier experimental studies over narrower temperature ranges. The TST treatment of Cohen and Westberg¹² gives good agreement with the experimental data at $T \gtrsim 400 \text{ K}$; when adjusted for tunneling through an Eckart barrier agreement extends down to 300 K.

A general point is that when modeling any H-atom transfer reaction with an appreciable energy barrier, it may be best to fit barrier heights at temperatures where tunneling should be relatively small and insensitive to the chosen parameters. The common procedure of fitting to k at $T = 300 \text{ K}$ must be done cautiously when k is small ($\leq 1 \times 10^{-14}$

cm³ molecule⁻¹ s⁻¹) because tunneling, which is difficult to quantify accurately, may make a large contribution there.

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