Figure 4. Curves of growth relative to the N_2O_5 1225–1270- cm^{-1} band and to the HNO_3 840–930- cm^{-1} band system (ν_5 , $2\nu_9$, $\nu_5 + \nu_9 - \nu_9$); 296 ± 2 K.

curve of growth analyses¹¹ for the N_2O_5 710–780- and 1225–1270- cm^{-1} bands and for the HNO_3 840–930- and 1270–1350- cm^{-1} bands. The calibration technique described in the Experimental Section for evaluation of the IBI values was also used in this case. Figure 4 shows two curves of growth for the N_2O_5 1225–1270- cm^{-1} band and the HNO_3 840–930- cm^{-1} band system.

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The S values were derived from a regression to the points in the linear region of the curve of growth. The results of this work are given in Table I along with existing literature data. The uncertainties associated with the values measured in this work were derived from the spread in the measured data and the estimated accuracy of the calibration procedure. A significant disparity is apparent between the N_2O_5 band strengths obtained in the present experiment and the values, measured by curve of growth analysis, given in ref 12. The comparison with the value measured for the 1225–1270- cm^{-1} band in ref 10 shows a much better agreement.

In the case of HNO_3 the comparison with the band strengths given in ref 13 and ref 15 shows that the values measured in the present experiment are lower by 17–19% for both bands. On the other hand, satisfactory agreement is apparent for the strengths of the 840–930- cm^{-1} band, measured in this work and in ref 14, the difference lying within the uncertainties of the determinations.

Acknowledgment. The authors gratefully acknowledge the contributions of Mr. G. Melandrone for the setup of the multipass cell-FTS system and of Mrs. H. Geiss for the ion chromatographic analysis.

Registry No. N_2O_5 , 10102-03-1; HNO_3 , 10102-43-9; H_2O , 7732-18-5.

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A High-Temperature Photochemistry Kinetics Study of the Reaction of $\text{O}(^3\text{P})$ Atoms with Ethylene from 290 to 1510 K

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(Received: June 13, 1986; In Final Form: September 24, 1986)

The $\text{O} + \text{C}_2\text{H}_4$ reaction has been investigated in a high-temperature photochemistry (HTP) reactor at temperatures from 290 to 1510 K and pressures from 60 to 500 Torr. Ground-state O atoms were generated by flash photolysis of CO_2 and monitored by time-resolved atomic resonance fluorescence with pulse counting. Measurements were made under pseudo-first-order conditions $[\text{O}] \ll [\text{C}_2\text{H}_4]$. Rate coefficients from 290 to 850 K are in good agreement with the numerous earlier measurements in that range. Above those temperatures a sharp rise in $k(T)$ with increasing T is evident. On the basis of present and other measurements by isolated elementary reaction techniques we recommend $k(T) = 1.3 \times 10^{-11} \exp(-830 \text{ K}/T) + 1.9 \times 10^{-9} \exp(-6940 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ as a fit expression for the 290–1510 K range. Confidence limits are discussed in the text. It is shown that the accepted transition-state treatment for channels significant at $T < 850$ K cannot account for the sharp upward curvature. Other channels will have to be considered at higher temperatures.

Introduction

Kinetic data on isolated elementary reactions covering wide temperature ranges and obtained in one apparatus are rare. Yet, such data are much desired to help arrive at a reliable experimental data base needed to improve our understanding of the influence of temperature on reactions. We have developed one such technique suitable for reactions involving species unstable with respect to collisions with high-temperature walls, the HTP (high-temperature photochemistry) technique.^{1,2} Here we report HTP measurements on the reaction

over the 290–1510 K range. The oxidation reactions of ethylene are a common subset in the combustion of higher molecular weight hydrocarbons, and the subsequent formation of acetylenic compounds is significant to soot formation.^{3,4} In recent years there have been several studies of reaction 1 to determine the temperature dependence of the rate coefficient in the 200–850 K range^{5–7} and to elucidate the reaction mechanism in that tem-

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Figure 1. Schematic diagram of the HTP reactor.

perature regime.⁵⁻¹³ The observations there can be attributed to intermediate formation of an O-atom adduct to the double bond

Among the product channels resulting from the addition reaction, $\text{H} + \text{CH}_2\text{CHO}$ and $\text{CH}_3 + \text{HCO}$ are the most significant at lower temperatures.¹⁴ However, at higher temperatures the only experimental information available on reaction 1 is derived from flame and shock tube studies, which require extensive modeling and hence are subject to considerable uncertainty. The aim of the present study has been to obtain direct measurements on the rate coefficients of the title reaction at higher temperatures under conditions $[\text{O}] \ll [\text{C}_2\text{H}_4]$ where secondary reactions can be excluded. We have concentrated on the 850–1510 K regime, but we have also included some measurements from 290 to 850 K to check for agreement with earlier work. Simultaneously with this study, Klemm et al.¹⁵ have made similar measurements covering the 240–1050 K regime.

Technique

1. Experimental Method. A schematic of the apparatus is shown in Figure 1. The HTP technique follows the same basic principles as the lower temperature flash photolysis–resonance fluorescence (FP–RF) technique, but ceramic and metal reactor construction parts are used to allow operation at temperatures as high as about 1800 K. A significant difference with FP–RF apparatus is the use of a movable cooled inlet system, which can reduce the residence time for thermally unstable species upstream of the reaction zone to periods on the order of 10^{-3} s and which creates an essentially wall-less reaction zone. The temperature inside the cooled inlet system can be maintained at 500 K at the highest reaction zone temperatures. A mixture of photolyte and reactant-in-excess (in this case, CO_2 and C_2H_4 , respectively) flow through the cooled inlet to mix with the heated bath gas Ar, upstream of the reaction zone. Photolysis pulses from the

Figure 2. Pseudo-first-order decay of O-atom fluorescence signal with background subtracted. Data at $P = 114$ Torr.

flashlamp generate O atoms. The CW resonance flow lamp is used to generate the fluorescence by which the decrease in $[\text{O}]$ is followed under pseudo-first-order conditions at a given pressure $P \approx [\text{Ar}]$, temperature T , and $[\text{C}_2\text{H}_4]$.

The reactor comprises an alumina tube, 5 cm diameter, and 91 cm long, situated in a steel vacuum chamber. It is heated over a 40 cm distance using silicon carbide spiral heating elements. Reaction zone temperature measurements are made using a retractable Pt/Rh thermocouple, doubly shielded to minimize radiation effects.¹⁶ Four perpendicular 2.4 cm diameter ports are aligned with 2.5 cm diameter windows on the vacuum chamber. The resonance flow lamp is powered by a 100-W CW microwave source and is equipped with a 2.5 cm diameter 15 cm focal length CaF_2 plano-convex lens to focus the exciting radiation and filter out the Lyman- α line. Further collimation is provided by 1 cm i.d. alumina rings in the flow lamp and PMT side arms.

The high-intensity capacitive discharge flash lamp consists of a 10 cm o.d. Plexiglas body, two 1 cm radius elkonite electrodes separated by a 4 cm gap and a 2.5 cm diameter MgF_2 window. The lamp operates on 100–500 Torr of N_2 at about 1 Hz. A 0.5 μF 25 kV capacitor delivers between 10 and 70 J per flash. A 555 timer chip controls the repetition rate of the flash. Five-volt square pulses are fed into an EG&G TM11-A trigger module, which initiates the flash on the rising edge of the square pulses. A photodiode on the flashlamp triggers the Nicolet 12/70 multichannel scaler on the falling edge of the flash to initiate data acquisition. The fluorescence is detected through a MgF_2 window by an EMI G-26E314LF photomultiplier tube. This PMT has a 1.6 cm diameter CsI photocathode and a MgF_2 window and is operated at 2600 V with a gain of 5×10^6 . The PMT signal is fed through an EG&G PAR 1121-A amplifier–discriminator to the multichannel scaler, the fluorescence decay information from which is transferred to an IBM personal computer for data handling.

CO_2 is photolyzed by the 120–167-nm portion of the flash continuum to yield predominantly $\text{O}(^1\text{D})$,^{17,18} which is rapidly quenched to $\text{O}(^3\text{P})$. The resonance lamp operates on He (99.999% U.H.P.), which, due to trace impurities, yields the O-atom 130.2–130.6-nm resonance triplet. The reactor gases (Linde) used are 99.998% Ar from liquid Ar, 1% and 0.1% C_2H_4 (99.5% c.p.) in Ar (99.998%, prepurified), and CO_2 (99.99% precision aquarator). In a few experiments O_2 (99.99% hydrocarbon-free U.H.P.) was used as photolyte instead of CO_2 . Flow and pressure measurements are made with Teledyne-Hastings digital flowmeters and an MKS baratron, respectively.

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TABLE I: Summary of Rate Coefficient Measurements on O + C₂H₄

T, K	P, ^a Torr	[M], 10 ¹⁸ cm ⁻³	[C ₂ H ₄], 10 ¹³ cm ⁻³	[CO ₂], 10 ¹⁵ cm ⁻³	$\bar{v}$, cm s ⁻¹	l, cm	F, J	$k \pm \sigma_k$, ^e 10 ⁻¹³ cm ³ molecule ⁻¹ s ⁻¹
293	112	3.69	(1.6–10) ^b	20	13	14.2	61	9.40 ± 0.44
295	259	8.48	(4.1–40) ^b	17 ^d	6	14.2	12	9.07 ± 0.15
296	115	3.75	(2.1–11) ^b	21	13	8.8	48	8.35 ± 0.14
328	101	2.97	(1.2–15) ^b	72	15	14.2	20	10.5 ± 0.5
332	101	2.94	(0.9–15) ^b	10 ^d	15	14.2	12	9.80 ± 0.45
392	60	1.48	(1.1–15) ^b	15	20	8.8	30	14.7 ± 0.7
405	102	2.43	(1.1–8.7) ^b	34	23	6.3	48	18.5 ± 0.5
413	203	4.81	(1.4–16) ^b	73	12	6.3	48	13.6 ± 0.9
465	110	2.29	(1.1–30) ^b	26	21	14.2	48	18.2 ± 1.1
548	250	4.41	(0.1–9.1) ^{b,c}	9	15	8.8	61	28.4 ± 1.0
554	202	3.61	(1.6–10) ^b	55	16	6.3	37	25.9 ± 1.0
613	500	7.88	(0.1–8) ^{b,c}	115	5	14.2	37	29.3 ± 1.4
702	318	2.38	(1.6–15) ^b	62	13	6.3	37	34.3 ± 2.0
707	177	2.42	(1.4–9.6) ^b	27	24	6.3	37	34.9 ± 2.2
844	405	4.63	(0.4–2.3) ^c	105	12	6.3	61	46.5 ± 1.1
848	314	3.58	(0.7–7.0) ^b	80	16	6.3	61	39.5 ± 0.9
861	240	2.69	(0.3–4.6) ^b	8	36	8.8	37	56.6 ± 5.6
904	500	5.34	(0.5–2.4) ^b	178	11	5.0	61	46.9 ± 1.6
912	306	3.24	(0.3–1.5) ^c	110	19	5.0	61	62.1 ± 5.1
953	103	1.04	(0.2–2.1) ^b	4.6	53	5.0	37	53.0 ± 2.8
967	400	3.99	(1.2–7.6) ^c	82	15	6.2	37	54.0 ± 1.4
1019	503	4.77	(0.4–2.2) ^c	75	12	5.0	48	54.0 ± 2.6
1028	320	3.01	(0.2–1.3) ^c	47	20	5.0	48	83.7 ± 4.9
1029	384	3.61	(0.6–1.8) ^c	77	15	5.0	37	60.7 ± 3.1
1036	382	3.56	(0.3–1.6) ^c	77	15	6.2	37	62.4 ± 5.2
1077	305	2.74	(0.2–1.3) ^c	93	21	6.2	37	79.5 ± 2.8
1083	305	2.71	(1.2–8.2) ^b	97	21	6.2	48	65.8 ± 3.9
1090	159	1.30	(0.4–3.7) ^b	83	42	6.2	48	68.2 ± 7.6
1125	169	1.45	(0.9–6.5) ^b	25	41	6.2	37	109 ± 9
1140	308	2.59	(0.2–1.2) ^c	40	23	3.7	37	100 ± 4
1150	308	2.59	(0.2–1.2) ^b	40	23	5.0	37	115 ± 3
1212	180	1.43	(0.6–5.3) ^b	33	40	6.2	37	160 ± 14
1258	501	3.85	(0.3–1.8) ^c	63	15	3.7	61	150 ± 10
1264	297	2.27	(0.1–1.0) ^c	36	26	3.7	37	140 ± 8
1330	430	3.12	(0.1–1.4) ^c	59	19	3.7	37	170 ± 11
1331	430	3.12	(0.5–3.5) ^b	55	37	3.7	61	229 ± 12
1397	114	0.76	(0.2–2.5) ^b	27	83	6.3	37	206 ± 8
1465	500	3.21	(0.3–4.3) ^b	63	27	3.7	58	208 ± 10
1490	364	2.69	(0.2–2.6) ^{b,c}	47	25	3.7	48	239 ± 19
1509	426	2.35	(0.07–0.9) ^c	42	33	3.7	70	245 ± 19

^a 1 Torr = 133.3 Pa. ^b 1% ethylene in argon. ^c 0.1% ethylene in argon. ^d O₂ used as photolyte instead of CO₂. ^e σ_k is based on random and systematic errors.

The average gas velocity and flash repetition rate are such as to allow essentially complete replenishment of the gas mixture in the reaction zone between flashes. Reaction zone residence times, however, are large compared to reaction times so that the reaction system may be assumed to be pseudo-static. Signals from between 100 and 1000 flashes are averaged to construct temporal profiles of the O-atom fluorescence intensity, such as Figure 2, at a given *T*, *P*, and [C₂H₄].

2. *Data Handling.* The measured O-atom fluorescence intensity decay plots, Figure 2, yield pseudo-first-order rate coefficients k_{ps1} based on the relation

$$-d \ln [O]_{rel}/dt = k_{ps1} = k[C_2H_4] + k_D \quad (2)$$

where [O]_{rel} is the [O] relative to the concentration of O at the end of the photolysis pulse, k_D represents essentially diffusional O-atom loss, and k is the rate coefficient of reaction 1 at the given *T* and *P*. In the calculation of k_{ps1} and associated standard deviations, errors in time are assumed to be negligible and each value of y_i (number of counts in any one channel) is assigned a variance equal to y_i following Poisson statistics. The points are assigned statistical weights, ω_i , proportional to the inverse of their respective variances, and initial estimates of the slope k_{ps1} and intercept I_0 are then made. An iteration procedure is then used which employs ω_i , k_{ps1} , and I_0 values obtained from the previous iteration to estimate new values of ω_i , k_{ps1} , and I_0 .¹⁹ The iteration

Figure 3. Plot of pseudo-first-order rate coefficient, k_{ps1} vs. [C₂H₄] yielding $k(1397\text{ K})$. Uncertainties shown are one standard deviation.

continues until the difference between two consecutive estimates of k_{ps1} is negligible. A goodness of fit test²⁰ is then used to determine whether the count data is of the form $I_0 \exp(-k_{ps1}t)$.

Plots of k_{ps1} against [C₂H₄], such as Figure 3, are then used to determine $k \pm \sigma_k$ values, Table I. Each line in that table thus corresponds to several k_{ps1} measurements, typically five to ten. Determination of σ_k requires an estimate of the uncertainty in [C₂H₄] values. To obtain these, statistical uncertainties in the flowmeter readings are estimated at 1.5% of full scale. An added

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1.5% error in calibration is allowed for. In view of these uncertainties, random and systematic errors¹⁶ in the pressure and temperature are found to have a negligible influence. By treating these uncertainties as standard deviations, concentration values and their variances are determined by a propagation of errors treatment. An iterative procedure is then used again to determine $k \pm \sigma_k$.^{2,21} Statistical weights ω_j proportional to $(\sigma_{k_{psl,j}}^2 + m^2 \sigma_{C_2H_4,j}^2)^{-1}$, where $\sigma_{k_{psl,j}}^2$, m , and $\sigma_{C_2H_4,j}^2$ denote variance in k_{psl} , estimate of slope, and variance in $[C_2H_4]$, respectively, are assigned to each point. The iteration continues until satisfactory convergence is obtained. Errors in both k_{psl} and $[C_2H_4]$ measurements are thus taken into account in determining a value for k and its variance.

To derive $k(T)$ expressions from the individual k values a weighted nonlinear least-squares fitting routine^{20,22} is used. σ_T is taken into account along with σ_k in the Newton-Raphson iterative procedure.²³

Results

Forty measurements of k were made from 290 to 1510 K. These are summarized in Table I. As shown there, experiments were performed over a wide range of $[M]$, $(0.76\text{--}8.5) \times 10^{18} \text{ cm}^{-3}$. The data reveal no consistent variation in results with $[M]$, showing the k values to be independent of pressure. The average gas velocity $\bar{v}$ was varied from 5 to 83 cm s^{-1} , the distance from the cooled reactant inlet tip to the center of the observed reaction zone l from 3.7 to 14 cm, and the flash lamp input energy F from 12 to 70 J to ascertain the absence of influence of these implicit experimental parameters on the obtained k values. The independence of the results of $\bar{v}$ and l , i.e., of residence time, indicates that thermal equilibrium between the bath gas Ar and the CO_2 and C_2H_4 flows had been achieved and that no significant pyrolysis of the C_2H_4 had occurred. However, at $T \geq 1300$ K we noticed that k values measured at residence times in excess of about 0.1 s were significantly smaller than those at shorter times. This may be attributed to heterogeneous decomposition of the ethylene. These measurements are therefore not included in Table I.

A number of fit expressions to the data of Table I have been attempted. The double-exponential equation

$$k(T) = (8.3 \pm 1.0) \times 10^{-12} \exp(-660 \pm 50 \text{ K}/T) + (2.8 \pm 1.6) \times 10^{-9} \exp(-7210 \pm 740 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (3)$$

gives a good fit²³ to the data set. In this expression the error limits in the parameter values are one standard deviation.

In Figure 4 the present k measurements are compared to other measurements by isolated elementary reaction techniques^{5-7,15} covering the lower part of the present temperature range. The agreement between these data is very satisfactory. The sharp increase in k with T , which has its onset at about 800 K, is also evident in the measurements by Klemm et al.¹⁵ Using all of these measurements we can now derive a new fit expression. Rather than evaluate the accuracy of the individual measurements of k we calculate a best unweighted fit:

$$k(T) = (1.3 \pm 0.1) \times 10^{-11} \exp(-830 \pm 30 \text{ K}/T) + (1.9 \pm 1.2) \times 10^{-9} \exp(-6940 \pm 830 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (4)$$

The error limits represent one standard deviation in each parameter. These limits can be combined with the covariances, using

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(23) Optimal values of the parameters were determined by minimizing χ^2 defined by

$$\chi^2 = \sum_{m=1}^{40} [\ln k_m - \ln \{A \exp(-B/T_m) + C \exp(-D/T_m)\}]^2 \omega_m$$

where

$$\omega_m = [(\sigma_{k,m}/k)^2 + (d \ln k/dT)^2 \sigma_T^2]$$

Here σ_T is estimated to be 10 K.

Figure 4. Comparison of present k values to other major measurements on the temperature dependence of the $O + C_2H_4$ rate coefficient above 290 K: (O) present study, 290–1510 K; (Δ) Perry,⁵ FP-RF, 260–860 K; ($\times$) Nicovich and Ravishankara,⁷ FP-RF, 300–810 K; ($\square$) Klemm et al.,¹⁵ FP-RF and discharge-flow reactor, 240–1050 K; ($\bullet$) Westenberg and deHaas,⁶ discharge-flow reactor with ESR, 195–715 K; (—) best fit; (---) Frank and Just,²⁵ shock tube, 1600–2300 K; (++++) Peeters and Mahnen,²⁶ flame, 1200–1700 K.

the method described by Wentworth,²⁴ to yield confidence limits for $k(T)$ at the 95% level of about $\pm 7\%$ for $T < 850$ K. The confidence limits rise to $\pm 18\%$ at 1510 K. Because the fit for $T \geq 850$ K is dominated by our data, we allow for possible systematic errors of 25% by increasing the confidence limits there to $\pm 30\%$. We favor this empirical double-exponential expression since it reproduces the strong upward curvature better than other standard expressions, such as $AT^n \exp(-B/T)$. The first term alone fits the low-temperature data very well and is close to that derived by Klemm et al.¹⁵

Equation 4 is the fit shown in Figure 4. Also given in that figure are shock tube²⁵ and flame²⁶ results. While these are in broad agreement with our measurements they suggest different temperature dependences. Such discrepancies, especially with flame studies, are not uncommon in view of the necessary assumptions regarding the other reactions occurring in those experiments.

Discussion

In order to evaluate the physical significance of the sharp rise in k above 800 K we use a transition-state theory (TST) treatment. For the regime $T < 850$ K, dominated by reactions 1a, k has been

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TABLE II: $\Delta S^\ddagger$ and $\Delta C_p^\ddagger$ for the Reaction $O + C_2H_4 \rightarrow OH + C_2H_3$ ^a

	$\Delta S^\ddagger_{300}$	$\Delta C_p^\ddagger_{p,400}$	$\Delta C_p^\ddagger_{p,800}$	$\Delta C_p^\ddagger_{p,1250}$
model molecule CH_2CHF	-30.5	-3.3	-3.1	-4.75
spin (triplet TS)	2.2			
translation	-0.13			
external rotation				
linear TS	2.19			
nonlinear TS	1.92			
1100 cm^{-1} C-F stretch $\rightarrow$ reaction coordinate	-0.05	-0.63	-1.45	-1.72
new O-H stretch, 2100 cm^{-1}	0	0.07	0.68	1.14
2 O-H-C bends, 600 cm^{-1} , linear TS	1.0	2.74	3.60	3.80
1 O-H-C bend and 1 internal rotor, nonlinear TS	0.5	1.37	1.80	1.90
	+3.6	+1.0	+1.0	+1.0
FCH bend, 1200 $cm^{-1} \rightarrow$ (O-H)•C bond, 700 cm^{-1}	0.3	0.70	0.37	0.20
F-C=C bend, 410 $cm^{-1} \rightarrow$ (O-H)•C=C bond, 270 cm^{-1}	0.6	0.17	0.05	0.03
total, linear TS	-24.39	-0.25	0.15	-1.30
total, nonlinear TS	-21.56	-0.62	-0.65	-2.20

^a All quantities in $cal\ mol^{-1}\ K^{-1}$.

Figure 5. Comparison of transition-state calculations to best fit of experimental data.

interpreted by a number of authors^{5,11,12,27} in terms of the expression

$$k_{1a} = (k_B T / h) [Q(CH_2CH_2 \cdot O^\ddagger) / \{Q(O) Q(C_2H_4)\}] \exp(-\beta / T) \quad (5)$$

This expression is commonly simplified by making two assumptions. These are that the temperature variation of the partition function for O atoms, $Q(O)$, is accounted for largely by the translational contribution $T^{3/2}$ and that the temperature dependences of $Q(CH_2CH_2 \cdot O^\ddagger)$ and $Q(C_2H_4)$ cancel except for the three new modes in the activated complex introduced by the addition of the O atom. One mode is factored out as the reaction coordinate

Figure 6. Calculated reaction pathways for the $O + C_2H_4$ reaction based on BAC-MP4 heats of formation for stable and transition-state structure species. Figure from Melius et al.³⁰ by permission.

and the other two correspond to degenerate $O \cdot C \equiv C$ bending with frequency ω (the single dot refers to a one-electron bond). This yields^{5,11}

$$k_{1a} = \alpha (T/K)^{-0.5} \{ (1 - \exp(-hc\omega/k_B T))^{-2} \exp(-\beta/T) \} \quad (6)$$

Explicit effects arising from the electronic partition function of $O(^3P)$, as discussed by Cohen and Westberg,²⁸ have been left out; the small contribution to the temperature dependence of $Q(O)$, an increase by a factor of 1.25 from 290 to 1510 K, is absorbed into the β term.

As Browarzik and Stuhl have noted,¹¹ for the case of O-atom addition to propene, satisfactory fits may be obtained with a wide range of ω values, 100–300 cm^{-1} in their case, while Perry⁵ gives 100–600 cm^{-1} . We select $\omega = 270\ cm^{-1}$ based on Benson's data for bending vibrations.^{29a} By requiring the calculated k_{1a} to agree with the average of the data in Figure 4 at 300 K and 500 K, 7.8×10^{-13} and $2.3 \times 10^{-12}\ cm^3\ molecule^{-1}\ s^{-1}$ respectively, we obtain $\alpha = 4.72 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ and $\beta = 567\ K$. Equation 6 is solved at several temperatures and the resulting values are fitted to the form $AT^n \exp(-B/T)$, giving

$$k_{1a} = 5.30 \times 10^{-16} (T/K)^{1.435} \exp(-267\ K/T)\ cm^3\ molecule^{-1}\ s^{-1} \quad (7)$$

which is shown in Figure 5. Clearly agreement with eq 4 for $T < 850\ K$ is excellent and slight non-Arrhenius behavior is evident in the addition channels. However, if an attempt is made to improve agreement at higher temperatures by fitting k_{1a} at 290 and 1510 K instead, then the resulting curve (Figure 5) is in poor agreement with the experimental data over much of the 290–1510 K range. This suggests that another channel becomes significant

(28) Cohen, N.; Westberg, K. R. *Int. J. Chem. Kinet.* **1986**, *18*, 99.(29) Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976. (a) Tables A.8. through A.18; (b) Chapters 2 and 4; (c) p 155.(27) Cvetanovic, R. J.; Singleton, D. L. *Rev. Chem. Intermed.* **1984**, *5*, 183.

TABLE III: Arrhenius Parameters for O + C₂H₄ → OH + C₂H₃ Derived from Transition-State Theory

	T, K			
	300	500	1000	1500
linear TS				
ΔS [‡] , cal mol ⁻¹ K ⁻¹	-24.39	-24.52	-24.42	-24.95
A, cm ³ molecule ⁻¹ s ⁻¹	8.81 × 10 ⁻¹²	2.29 × 10 ⁻¹¹	9.65 × 10 ⁻¹¹	1.66 × 10 ⁻¹⁰
ΔH [‡] , cal mol ⁻¹	3670	3620	3690	3040
E _a , cal mol ⁻¹	4860	5600	7660	9000
k _{8L} , cm ³ molecule ⁻¹ s ⁻¹	2.6 × 10 ⁻¹⁵	8.2 × 10 ⁻¹⁴	2.0 × 10 ⁻¹²	8.1 × 10 ⁻¹²
nonlinear TS				
ΔS [‡] , cal mol ⁻¹ K ⁻¹	-21.56	-21.88	-22.33	-23.22
A, cm ³ molecule ⁻¹ s ⁻¹	3.66 × 10 ⁻¹¹	8.66 × 10 ⁻¹¹	2.76 × 10 ⁻¹⁰	3.97 × 10 ⁻¹⁰
ΔH [‡] , cal mol ⁻¹	7190	7060	6740	5640
E _a , cal mol ⁻¹	8380	9050	10710	11600
k _{8N} , cm ³ molecule ⁻¹ s ⁻¹	2.9 × 10 ⁻¹⁷	9.6 × 10 ⁻¹⁵	1.3 × 10 ⁻¹²	8.1 × 10 ⁻¹²

above 850 K. The rate coefficient k_8 for this postulated channel must have both a larger activation energy and a larger preexponential factor than k_{1a} . Melius has made ab initio thermochemical calculations using the BAC-MP4 method on the O + C₂H₄ system,³⁰ results of which are shown in Figure 6. From this figure, the abstraction reaction

would be a logical candidate, based on the high activation energy. To test this hypothesis TST calculations have been carried out employing the principles outlined by Benson^{29b} to estimate properties of the CH₂CH(HO)[‡] transition state, TS. Tables II and III summarize the results.

CH₂CHF was selected as a model compound for the TS. C[∞]_{P,1500} was approximated by fitting a quadratic function of T to available data^{29a} and extrapolating. The contribution of spin to ΔS[‡]₃₀₀ was taken to be similar to that for Benson's example for O + C₂H₆ → OH + C₂H₅.^{29c} Following this example two different TS's were investigated, the linear case and one where the C–H–O angle was 150°. To estimate changes in moments of inertia the bond lengths and angles for ethylene³¹ were combined with bond lengths for C–F^{29a} and C–H–O²⁸ in the TS. Contributions to ΔS[‡]₃₀₀ from the internal rotor in the nonlinear TS were assumed to be equal to those for O + C₂H₆^{29c} and O + CH₄.³² The kinetic parameters A and E_a , defined by $E_a = -d \ln k_8/d(1/T)$ and $k_8 = A \exp(-E_a/RT)$, were obtained from ΔS[‡] and ΔH[‡] by using³³

$$A = 2.098 \times 10^{-11} (T/K)^2 \exp(\Delta S^\circ / R) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (9)$$

$$E_a = \Delta H^\circ + 2RT \quad (10)$$

(30) Melius, C. F.; Binkley, J. S.; Koszykowski, M. L., private communications, May 1984 and March 1986.

(31) JANAF Tables; Dow Chemical Co., frequently updated.

(32) Golden, D. M. *J. Phys. Chem.* **1979**, *83*, 108.

ΔS[‡] was calculated for 300–1500 K and ΔH[‡]₁₅₀₀ adjusted so that k_8 equaled the observed difference between k_{1a} and k at 1500 K. ΔH[‡] and hence k_8 were then extrapolated to lower temperatures. The nonlinear model gives

$$k_{8N} = 1.18 \times 10^{-15} (T/K)^{1.55} \exp(-3770 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (11)$$

while the linear model gives

$$k_{8L} = 2.50 \times 10^{-17} (T/K)^{1.91} \exp(-1880 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (12)$$

where these parameterized expressions lie within 2% of the calculated points (Table III). The sums $k_{1a} + k_{8N}$ and $k_{1a} + k_{8L}$ are plotted on Figure 5. There is somewhat better agreement between experiment and TST for the nonlinear model, although both curves lie above the observed data at $T \approx 1000$ K.

It is therefore plausible that another channel, not apparent from the current BAC-MP4 calculations,³⁰ may contribute to O-atom removal, together with or instead of H-atom abstraction. A more detailed theoretical treatment including not only the triplet surface described there,³⁰ but also a singlet surface, would be desirable.

Acknowledgment. This work was supported by the Department of Energy, Office of Basic Energy Sciences, Dr. A. H. Laufer, Technical Monitor, under Grant DE-FG02-84ER13224. We thank W. F. Flaherty for his dedicated help with the experiments and D. F. Rogowski, G. C. Billiard, and R. C. Hahn for technical assistance. The advice and interest of Drs. R. B. Klemm and J. V. Michael is gratefully acknowledged. We thank Drs. C. F. Melius et al. and R. B. Klemm et al. for communicating their data before publication.

Registry No. CH₂=CH₂, 74-85-1; O, 17778-80-2.

(33) Golden, D. M. *J. Chem. Educ.* **1971**, *48*, 235.