Temperature Dependence of the Rate Constants of the Reactions of OH Radicals with C_2H_2 and C_2D_2 at 1 atm in Ar and from 333 to 1273 K[†]

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The absolute rate constants for the gas-phase reactions of $OH + C_2H_2$ and $OH + C_2D_2$ were measured at a total pressure of 1 atm in argon buffer gas from 333 to 1273 K by using the pulse radiolysis technique. The predominant reactions were found to change from the addition reaction at lower temperatures to the H-atom abstraction reaction at higher temperatures. The kinetic isotope effect of k(H)/k(D) was ≈ 1 below 393 K, <1 from 393 to 1073 K, and >1 above 1073 K. From the experimental data of this work and the previous investigations, the second-order rate constant for addition reaction could be expressed as $8.5 \times 10^{-12} e^{(-1400 \pm 60)/RT}$ cm³ molecule⁻¹ s⁻¹ and for H-atom abstraction reaction as $4.5 \times 10^{-11} e^{(-10500 \pm 3100)/RT}$ cm³ molecule⁻¹ s⁻¹. The indicated error limit in the Arrhenius activation energy is 1 standard deviation of the least-squares analysis.

Introduction

The reaction of hydroxyl radical with acetylene is a very important reaction in both combustion and atmospheric chemistry and has been studied by many techniques over a wide range of pressures and temperatures.¹⁻¹⁶ The experimental results have revealed the complexity of this reaction. The predominant reactions are temperature and pressure dependent.

The pressure dependence of the overall rate constants measured at low temperatures (<429 K)^{7,10-12} indicated the importance of the addition reaction channel. The mechanism for these addition-initiated reactions could be expressed as¹⁶

OH + C₂H₂
$$\frac{k_1}{k_{-1}}$$
 [CH=CHOH][†] (1, -1)

$$[CH=CHOH]^{\dagger} + M \xrightarrow{\kappa_2} CH=CHOH + M \qquad (2)$$

Under low-pressure conditions, the mechanism becomes more complex, and the isomerization of the energy-rich adduct and subsequent decomposition could compete with reactions -1 and 2:16

$$[CH = CHOH]^{\dagger} \xrightarrow{k_{\text{loom}}} [CH_2CHO]^{\dagger} \rightarrow CH_2CO + H \quad (\text{isom})$$

At room temperature there is reasonable agreement between the different measurements that have been carried out over a range of pressures greater than 150 Torr^{5-7,9-12} and reported as at (or close to) the high-pressure limit value. Above room temperature, however, differences appear. Perry and Williamson¹⁰ measured rate constants up to 429 K at about 200 Torr and reported an Arrhenius expression for the high-pressure limit as $k = 1.55 \times$ $10^{-12}e^{-485/RT}$ cm³ molecules⁻¹ s⁻¹ using their data and that of Perry et al.¹² However, Michael et al.¹¹ reported $k_{\infty} = (6.83 \pm 1.19)$ $\times 10^{-12} e^{(-1284 \pm 93)/RT}$ cm³ molecule⁻¹ s⁻¹ over a wider pressure range (300-600 Torr at 362 K and 450-1100 Torr at 413 K). In a recent review, 16 Atkinson recommended the equation of 1.90 \times $10^{-12}e^{-(465\pm252)/RT}$ cm³ molecule⁻¹ s⁻¹ for the high-pressure limit. More measurements at low temperatures and high pressures would be helpful in explaining the disparate results.

Above 900 K several early flame studies indicated the importance of the H-atom abstraction reaction:^{14,15} L.

$$C_2H_2 + OH \xrightarrow{\gamma} C_2H + H_2O$$
 (3)

Recently, Smith et al. directly measured the OH-acetylene reaction at 900, 1100, and 1300 K using a laser pyrolysis/laser fluorescence technique and reported that there was a pressure effect at 900 K (total pressures were 50-224 Torr) and no pressure effect at 1100 K (total pressures were 43-349 Torr) and 1300 K (total pressures were 100-160 Torr).⁸ They suggested that the predominant pathway had switched to H-atom abstraction in the range 1000-1400 K.⁸ Because of the importance of the hydrogen abstraction reaction at the combustion temperatures, more measurements both at high temperatures and at the pressures close to combustion conditions are needed.

In the intermediate region (429-900 K), no direct measurements have been reported. The present measurements in this intermediate temperature regime provide a useful insight into the details of the reaction and an experimental counterpart to the theoretical RRKM calculations of Smith et al. Those calculations might be expected to be accurate to within a factor of 2.8

For the above-mentioned reasons, a pulse radiolysis study has been carried out at 1 atm and over the temperature range 333-1273 K for the reaction of OH with acetylene and 358-1173 K for OH with deuterioacetylene.

Experimental Section

The experimental details have been described previously,¹⁷⁻¹⁹

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Figure 1. Typical OH decay profile during the reaction with C_2H_2 at 423 K. The concentration of C_2H_2 in the reaction cell was 3.7×10^{15} molecules cm⁻³. The solid line is the nonlinear least-squares fit to the pseudo-first-order reaction.

and only the basic principles and changes to the system will be described here. A flow system was used for this experiment, and the composition of the sample was controlled by varying the flow rates of the reactants (flowing at 0.0005-0.01 L/min (STP)) and the buffer gas (argon at 1 L/min (STP) and containing about 6 Torr of water). The reaction cell was heated by an oven, and the temperature was measured at the outlet of the cell and controlled within $\pm 2 \text{ K}$.

The gas mixture was irradiated in the cell with an electron beam (15 MeV, 0.25–3 μ s, peak current 1.5 A), which ionized the argon. The ion-recombination and further reactions give Ar* and Ar₂*. These species transfer energy to the water, decomposing it to form H and OH. From the maximum absorption of the OH radical and from the rate of disappearance of OH through a second-order reaction with itself, the initial concentration of OH was estimated to be $10^{12}-10^{13}$ molecules cm⁻³.

Resonance absorption was used to measure the OH concentration. A microwave discharge in water-helium was used to generate the OH resonance line (308 nm). The resonance line was isolated by using an interference filter and detected by using a photomultiplier (Hamamatsu R928 with five dynodes). The output of the photomultiplier was digitized by using a Biomation 8100 transient recorder and accumulated and averaged in a computer (DEC 11/23).

The argon used in this study was UHP grade, 99.999%, from Matheson Gas Products Inc. An acetylene mixture of 50.97% C_2H_2 (purified, 99.6% minimum) in UHP argon was made by Matheson. Acetylene- d_2 was obtained from ICN Biomedicals, and the mixture with UHP argon was made by Matheson. Mass spectroscopic analysis indicated that in the 16.8% C_2D_2 sample there were 15.0 ± 0.5% of C_2D_2 and 1.8 ± 0.2% of C_2DH . The concentration of reactants in the reaction cell was on the order of 10^{15} - 10^{16} molecules cm⁻³, which was at least 2 orders of magnitude greater than the concentration of OH. This was necessary for a pseudo-first-order reaction.

Results and Discussion

The measurements were performed over the temperature range 333-1273 K for the C_2H_2 reactions and 358-1173 K for C_2D_2 . A typical OH decay profile is shown in Figure 1. The data were fit to an exponential decay by using a nonlinear least-squares fitting program. The fit of the data in Figure 1 is shown by the solid line. Exponential decays for OH were observed under all conditions for times less than 1 ms. Typical plots of the measured pseudo-first-order rate constant k' versus concentration are given in Figure 2 (for C_2H_2) and Figure 3 (for C_2D_2). The intercept



Figure 2. Several examples of the measured pseudo-first-order rate constant k' of OH + C₂H₂ versus concentration of C₂H₂ in the reaction cell. The data at 363 K were moved down 3000 s⁻¹ for clarity.



Figure 3. Several examples of the measured pseudo-first-order rate constant k' of OH + C₂D₂ versus concentration of C₂D₂ in the reaction cell. The data at 358 K were moved down 3000 s⁻¹ for clarity.

of these plots is primarily attributed to second-order reactions of OH with generated radicals (including OH and decomposition products from acetylene). This was confirmed by making measurements where the initial concentration of OH was decreased by a factor of 10. The intercept of plots similar to Figures 2 and 3 was decreased; however, the slope and thus the second-order rate constant were unaffected. In previous work the data had been fitted by including the second-order decays generated by OH and the products of the reaction of an additive gas with excited argon.¹⁹ These studies showed that the intercept was eliminated and that the second-order rate constant determined was the same as that which would be determined by using the technique used in the present work.

The total experimental uncertainties were estimated to be about $\pm 10\%$.¹⁷ Because there were small concentrations of C₂DH in the C₂D₂ samples, the rate constants for the C₂D₂ reaction were calculated by assuming that the rate constant of C₂DH is between that of C₂D₂ and C₂H₂. The difference between the corrected and measured values is less than $\pm 10\%$, and the corrected values are given here.

All rate constants are given in Table I and plotted in Arrhenius form in Figure 4. Data from previous studies are collected in Table II and also plotted in Figure 4.

Figure 4 shows that at room temperature there is reasonable agreement between different measurements that have been done at total pressures above 150 Torr and were assumed to be the high-pressure limit value.^{5-7,10-12} Our measurements at low temperatures (<393 K for C_2H_2 and <573 K for C_2D_2) are in good agreement with the high-pressure limit data of Michael et al.,¹¹ who reported on experiments over a wide pressure range (from

⁽¹⁹⁾ Jonah, C. D.; Mulac, W. A.; Zeglinski, P. J. Phys. Chem. 1984, 88, 4100.

TABLE I: Absolute Rate Constants of OH + C_2H_2/C_2D_2 Reactions Measured in This Work by Pulse Radiolysis Resonance Absorption at Total Pressure of 1 atm of Argon^a

$OH + C_2H_2$		$OH + C_2D_2$					
$10^{13}k$	<i>T</i> , K	$10^{13}k$					
10.5	358	12.6					
12.3	383	13.2					
12.6	443	19.3					
13.5	448	18.4					
14.6	478	21.8					
14.2	573	19.7					
13.7	673	17.5					
13.4	773	17.3					
14.1	878	10.5					
10.8	1073	4.80					
9.18	1173	5.30					
5.95							
5.25							
5.48							
6.40							
5.83							
6.87							
8.69							
11.7							
	$\begin{array}{r} \hline C_2H_2 \\ \hline 10^{13}k \\ \hline 10.5 \\ 12.3 \\ 12.6 \\ 13.5 \\ 14.6 \\ 14.2 \\ 13.7 \\ 13.4 \\ 14.1 \\ 10.8 \\ 9.18 \\ 5.95 \\ 5.25 \\ 5.48 \\ 6.40 \\ 5.83 \\ 6.87 \\ 8.69 \\ 11.7 \\ \hline \end{array}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $					

^aThe overall accuracy of this experiment is $\pm 10\%$. Rate constants are in the unit of cm³ molecule⁻¹ s⁻¹.

10 to 1100 Torr) and found that at higher temperatures the high-pressure limit was obtained at higher total pressures. Because Michael's measurements were made at higher pressures, they are probably more reliable estimates of the high-pressure limit of the addition rate constant than the measurements made at lower pressures. The amount that one might expect our measurements to vary from the high-pressure limit can be estimated from the calculations of Smith et al.⁸ as shown in Figure 8 of their paper. The difference between the 750-Torr data and the high-pressure limit does not become significant until the temperature is greater than 450 K. The dashed line in Figure 4 represents their RRKM calculation for the temperature dependence of the rate at 760 Torr and is in good agreement with the present data for temperatures less than about 725 K. The deviation at higher temperatures might well be due to an uncertainty in β , the collision energy-transfer parameter, as a function of temperature. The kinetic isotope effect observed in this work $(k(H)/k(D) \approx 1$ below 393 K) also suggests that below 393 K the addition reaction of OH with C_2H_2 is near the high-pressure limit at 1 atm. At higher temperatures (up to



Figure 4. Arrhenius plot of the absolute rate constants of $OH + C_2H_2$ (O) and $OH + C_2D_2$ (\bullet) measured in this work. Several data of $OH + C_2H_2$ from the literatures are also plotted by using different symbols, which are explained in the Table II. The solid line *I* is the least-squares fit to the high-pressure limit data of addition reaction. The solid line *II* is the least-squares fit to the data of hydrogen-abstraction reaction. The dashed line *III* is the RRKM calculation for the addition reactions at 760 Torr of total pressure from Smith et al.⁸ (See text for details).

573 K) the C_2D_2 reaction was still not far from the high-pressure limit (see the discussion below). Combining all previous room temperature data from Table II and all data of Michael et al.¹¹ with our low-temperature measurement, a linear fit would give an Arrhenius expression for the high-pressure limit rate constant as $8.5 \times 10^{-12} e^{(-1400 \pm 60)/RT}$ cm³ molecule⁻¹ s⁻¹, where the indicated error limit in the Arrhenius activation energy is 1 least-squares standard deviation. This expression is plotted in Figure 4 as line I. The activation energy of the addition reaction then is about 1.4 kcal mol⁻¹, and a large temperature dependence would be expected. This expression is very close to the expression of Michael et al.¹¹ but not in agreement with that of Perry et al.^{10,12} and Atkinson's recommendation¹⁶ (see above). The disagreement here may imply that the measurements of Perry et al. at the temperatures above 300 K were not in the high-pressure limit. Note also that Smith et al.8 had difficulties simulating the data of Perry et al.10

TABLE II: Summary of the Rate Constant of OH + C_2H_2 Reaction from the Literature (All Rate Constants Are in the Units of cm³ molecule⁻¹ s⁻¹)

,					
Т, К	10 ¹³ k	technique ^a	total pressure	ref	symbol in Figure 4
297	8.80 ± 2.0	relative	1 atm air	Hatakeyama et al. ⁵ (1986)	φ
295	$8.3 \pm 0.8 \ (k_{\infty})$	LP-LF	1 atm He, Ar, N ₂	Schmidt et al. ⁶ (1985)	I
298	9.0 (k_{∞})	LP-RA	$10-1000 \text{ mbar } N_2$	Wahner et al. ⁷ (1985)	+
1100	2.7 ± 0.6	LP-LF	43-349 Torr mixture	Smith et al. ⁸ (1984)	0
1300	5.8 ± 0.8	LP-LF	100-160 Torr mixture	Smith et al. ⁸ (1984)	0
298	8.8 ± 1.4	relative	1 atm air	Atkinson et al. ⁹ (1984)	
297	6.75 ± 0.70	FP-RF	>200 Torr Ar	Perry et al. ¹⁰ (1982)	Δ
429	7.98 ± 0.90	FP-RF	>200 Torr Ar	Perry et al. ¹⁰ (1982)	Δ
228	3.84 ± 0.25	FP-RF	10-100 Torr Ar	Michael et al. ¹¹ (1980)	×
257	5.97 ± 0.50	FP-RF	75-200 Torr Ar	Michael et al. ¹¹ (1980)	×
298	7.76 ± 0.73	FP-RF	150-600 Torr Ar	Michael et al. ¹¹ (1980)	×
362	10.56 ± 1.56	FP-RF	300-600 Torr Ar	Michael et al. ¹¹ (1980)	×
413	14.99 ± 1.63	FP-RF	450-1100 Torr Ar	Michael et al. ¹¹ (1980)	×
298.1	6.79 ± 0.70	FP-RF	>200 Torr Ar	Perry et al. ¹² (1977)	۵
350.2	7.63 ± 1.00	FP-RF	>200 Torr Ar	Perry et al. ¹² (1977)	Δ
422.4	9.26 ± 1.20	FP-RF	>200 Torr Ar	Perry et al. ¹² (1977)	۵
570-850	$5.3 \times 10^{-13} e^{-200/RTb}$	flame	40 torr	Vandooren et al.13 (1977)	
650-1100	$9.1 \times 10^{-11} e^{-13700/RTc}$	flame	40 torr	Vandooren et al. ¹³ (1977)	
1500-1600	$1 \times 10^{-11} e^{-7000/RTd}$	flame		Browne et al. ¹⁴ (1969)	
at 1550	10.5			Browne et al. ¹⁴ (1969)	∇
1700-2000	33.2	flame		Fenimore et al. ¹⁵ (1964)	o

^aRelative: relative study taking $k(OH + cyclohaxane) = 7.57 \times 10^{-12} \text{ cm}^3$ molecule⁻¹ s⁻¹; LP-RA, laser photolysis resonance absorption; LP-LF, laser photolysis (pyrolysis) laser-induced fluorescence; FP-RF, flash photolysis resonance fluorescence. ^bFor reaction C₂H₂ + OH \rightarrow C₂H₂O + H. ^cFor reaction C₂H₂ + OH \rightarrow CH₃ + CO. ^dFor reaction C₂H₂ + OH \rightarrow C₂H + H₂O, one point (∇) was taken at 1550 K.

Above 393 K and at 1 atm, the fall-off of the overall reaction for C_2H_2 becomes significant. Because of the statistical weight effects for unimolecular decomposition of the adduct in the nonequilibrium situation, an inverse isotope effect of k(H)/k(D)< 1 would be expected,²⁰ which is consistent with our observations from 393 to 1073 K. The fall-off for C₂D₂ appeared above 573 K, which is 160 K higher than the corresponding temperature for C_2H_2 . In both cases the rate constants showed complex behavior, i.e., first it become almost constant (a plateau) and then falls drastically. This is very similar to the result of the RRKM study of Smith et al.8 Their calculated result for addition reactions at 760 Torr of total pressure is shown in Figure 4 as a dashed line III (for details about this RRKM calculation see Figure 8 in ref 8). There is a good agreement between our experimental measurements and their theoretical prediction except that the experimental data show the sharp decreasing of rate constants at lower temperatures than that of calculation. But if one considers the experimental error limit ($\approx \pm 10\%$) and the estimated accuracy of that RRKM calculation (a factor of 2 (ref 8)), the agreement is satisfactory. The data of the OH/C_2D_2 reaction reported here may also provide an opportunity to check the theory and to get more information about the transition-state structure of the energy-rich adduct. With the positive temperature dependence of the addition reaction, the overall rate constant is greater than $k_{\infty}(300 \text{ K})$ for temperatures up to 723 K and of comparable value $(>0.5k_{\infty}(300 \text{ K}))$ at even higher temperatures. This is consistent with the prediction of Smith et al.⁸ and Michael et al.¹¹

Above 1073 K, the rate constants for both C_2H_2 and C_2D_2 increase with increasing temperature, and a normal kinetic istope effect of k(H)/k(D) > 1 has been observed. This supports the assertion of Smith et al.8 that the predominant reaction switches from addition-initiated reactions to H-atom abstraction at elevated temperatures. A similar temperature dependence has been observed in previous studies of OH with ethylene¹⁷ and propylene.^{21,22} This may be a common behavior for reactions of OH radicals with unsaturated hydrocarbons. Recently a similar transition was seen for vinyl chloride, propylene, and 1-butene,²³ but it was not seen for allene and 1,3-butadiene.²⁴ The failure was due to the high addition reaction rate in 1,3-butadiene at atmospheric pressure and other pathways for the energy-rich adduct in the allene case.

The rate constants of OH with C_2H_2 measured by this work at 1073-1273 K are larger than the measurements of Smith et al. by a factor of 2. It is hard to explain this difference with the available experimental results. It does not seem to be due to the pressure effect of the addition reaction channel at that temperature range. The drastic decrease of the rate constants measured in the present work over the temperature range from 723 to 973 K would predict that the rate constant for addition-initiated reactions at a total pressure of 1 atm would decrease to less than 1×10^{-13} cm³ molecule⁻¹ s⁻¹ for temperatures above 1000 K. Clearly, more experiments at different pressures around 1000-1300 K are

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necessary for explaining this difference. At present, however, we will use all available high-temperature data to get the Arrhenius parameters for the hydrogen-abstraction reaction. The combination of high-temperature data of Browne et al.,¹⁴ Fenimore and Jones,¹⁵ Smith et al.,⁸ and our results for C₂H₂ above 1073 K gives an Arrhenius expression for the H-atom abstraction of 4.5 \times $10^{-11}e^{(-10500\pm3100)/RT}$ cm³ molecule⁻¹ s⁻¹, where the indicated error limit in the Arrhenius activation energy is 1 standard deviation. This expression is shown in Figure 4 as line II. It is close to the expression obtained by Smith et al.⁸ (2 \times 10⁻¹¹ $e^{-9000/RT}$ cm³ molecule⁻¹ s⁻¹) and indicates a large activation energy (about 10 kcal mole⁻¹) for the hydrogen abstraction from acetylene by OH radicals.

Previous studies^{5-7,11,13,16} discussed the possible pathways other than the mechanisms of (1, -1)-(3). Among these discussions, the regeneration of OH in the reaction of $OH + C_2H_2/O_2$ system and OD formation in the reaction of $OH + C_2D_2/O_2$ system are most interesting.⁵⁻⁷ To see if these reactions occurred in the absence of oxygen and at around atmospheric pressures, we carried out a similar experiment. We attempted to observe the formation of OH in the reaction of OD + C_2H_2 and OD formation in the reaction of $OH + C_2D_2$ at 323 and 653 K. No formation was observed. With a small amount of oxygen (0.005 L/min (STP) of 100% O_2), there still was no formation detectable within the sensitivity of this experiment (minimum detectable concentration of OH is 5×10^{10} molecules cm⁻³, which is about 1% of a normal signal). The only evidence for the regeneration of OH in the reaction of $OH + C_2H_2/O_2$ is that the measured rate constants for OH disappearance were lower than that in the absence of oxygen.

Conclusion

The temperature dependence of the reaction of $OH + C_2H_2$ and C_2D_2 at 1 atm of total pressure in argon buffer gas was studied from 333 to 1273 K. The predominant reactions were found to be temperature dependent. At atmospheric pressure, below 393 K, the kinetic isotope effect \approx 1, which implies the addition reaction is close to the high-pressure limit. In the temperature range 393-1073 K the inverse kinetic isotope effect indicated the importance of the addition/stabilization/back-decomposition reactions, and it seems no other reaction channels were important at this pressure. Above 1073 K, the H-atom-abstraction reaction becomes more important, and a normal kinetic isotope effect was observed.

Because this experiment has been done at a constant total pressure and only the OH disappearance was observed, measurements as a function of pressure are needed, particularly at the higher temperatures. Product analyses at different temperatures and pressures are needed to understand the detailed mechanisms.

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