Flash photolysis-resonance fluorescence kinetics study: Temperature dependence of the reactions OH + CO → CO$_2$ + H and OH + CH$_4$ → H$_2$O + CH$_3$

D. D. Davis, S. Fischer, and R. Schiff

Chemistry Department, University of Maryland, College Park, Maryland 20742
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Two reactions involving the transient chemical species OH($v'' = 0$) and the reactants CO and CH$_4$ have been investigated over a temperature range of nearly 140°C. Of particular importance were the measurements made below 300°C where data has heretofore been lacking. The rate constant expressions in Arrhenius form are $k_{CO} = (2.15 \pm 0.19) \times 10^{-13} \exp[-(160 \pm 80 \text{ cal mol}^{-1})/R\,T]$ and $k_{CH_4} = (2.36 \pm 0.21) \times 10^{-12} \exp[-(3400 \pm 175 \text{ cal mol}^{-1})/R\,T]$. Units are cm^3 mol^{-1} · sec^{-1}. Wide variations in the total pressure, H$_2$O concentration, initial OH concentration, and the nature of the diluent gas showed no indication of complex secondary reactions. The activation energies reported in this work for both processes, virtually zero for Reaction (1) and 3400 cal mol^{-1} for Reaction (2), are incompatible with those same quantities previously reported at elevated temperatures and indicate either nonlinear Arrhenius behavior for these OH reactions or possibly errors in experimental measurements.

INTRODUCTION

Two hydroxyl radical reactions which have long been recognized as of considerable importance in studies of atmospheric and combustion processes are:

$$OH + CO \rightarrow CO_2 + H \qquad (1)$$

and

$$OH + CH_4 \rightarrow CH_3 + H_2O \, . \qquad (2)$$

Reaction (1) has been shown to be the major sink mechanism for the conversion of CO to CO$_2$ in the atmosphere,[1] and the importance of Reaction (2) in atmospheric kinetics is that it constitutes the primary mode through which CH$_4$ is degraded to CO.[2] In the case of combustion processes, methane has been used as a model hydrocarbon in the elucidation of kinetic processes involved in diffusion controlled flames.[3] Reaction (2) is a key initiator in the degradation of CH$_4$, and Reaction (1) is similarly important in the oxidation of the CO to CO$_2$ under combustion conditions.

In spite of the numerous studies of Reactions (1) and (2) performed over the last ten years, many discrepancies in the reported results still remain. Over this time period, for example, the activation energy for Reaction (1) has varied by a factor of 30 and that for Reaction (2) by a factor of four.[4] At least part of this variability has been due to the fact that the bulk of the work on these systems has been done at high temperatures, in flame studies. A major problem encountered in this difficult area of investigation is the large number of secondary processes which can become significant at elevated temperatures. Thus, perturbations in the OH concentration are more probable, and significant errors in the measurement of rate parameters under these conditions are likely to occur.

More recently of particular significance has been the large discrepancy which exists in the correlation of the high and low temperature data for Reaction (1). As seen in Fig. 1, nonlinear Arrhenius behavior is indicated when the high and low temperature data are combined. The recent work by Westenberg and deHaas[5] also shows curvature over the temperature range 298°–915 °K and does not agree with the previous work of Greiner.[6] The possibility of non-Arrhenius behavior for Reaction (1) makes it imperative that this reaction be studied over as wide a temperature range as possible. As of this writing, no studies of Reaction (1) have been performed at temperatures of less than 298 °K. A similar situation also exists for Reaction (2). The present work, therefore, represents an attempt to extend the useful working range of temperature on both of these important systems. The technique employed in both cases is that of flash photolysis-resonance fluorescence. Reaction (1) has been investigated over the temperature range of 220 –373 °K, and Reaction (2) over the temperature range of 240 – 373 °K.

EXPERIMENTAL

The flash photolysis-resonance fluorescence technique used in this study has been described previously,[7,8] and only those modifications which were made to adapt the system for measurements of OH will be discussed here in any detail.

The cell used in these studies was constructed of aluminum, and was black anodized to reduce scattered light. The total volume of the cell was approximately 850 cm^3. The reaction cell temperature was controlled by passing a heated or cooled fluid through channels cut in the walls of the reaction cell. The precision in obtaining temperatures > 273 °K was estimated to be ± 0.2 °K or better, while at temperatures below 273 °K the precision was ± 1.5 °K or better. The resonance lamp, of the same design as Davis and Braun,[9] was fitted with a Suprasil quartz window ($\lambda \geq 1650$ Å), and the OH emission lines were generated by flowing a 2% H$_2$O/Ar mixture through the lamp at a total pressure of approximately 600 mtorr. The resonance fluorescence was monitored via a photomultiplier tube (RCA type 8850)
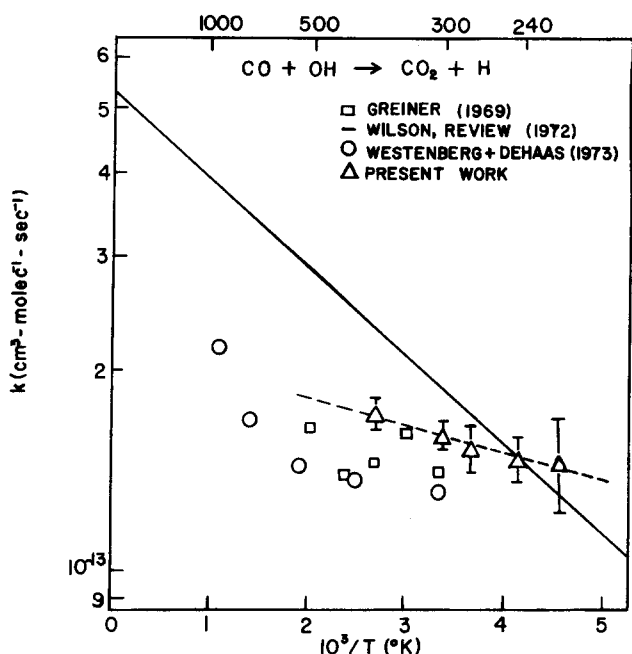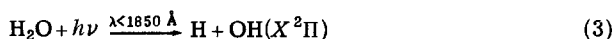
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FIG. 1. An Arrhenius plot showing the temperature dependence of the reaction of OH with CO.

which was mounted perpendicular to the resonance lamp.

Several tests were performed to characterize the OH resonance lamp to determine the relative intensities of various possible spectral bands. The first test involved the placement of a 3070 Å interference filter (200 Å half-bandwidth) over the photomultiplier tube in order to limit the light detected to the $(A\ ^2\Sigma^+;\ \nu'=0) \rightarrow (X^2\Pi;\ \nu''=0)$ transition of OH. Since photon counting techniques are used in our experimental system, the resonance lamp intensity in this spectral region was measured in the form of a count rate. Following this test, the 3070 Å filter was replaced by a 3450 Å interference filter which could detect the presence of radiation corresponding to the OH transition $(A^2\Sigma^+;\ \nu'=0) \rightarrow (X^2\Pi;\ \nu''=1)$. When appropriate corrections for differences in transmission and bandwidth of the 3450 and 3070 Å filters as well as differences in the quantum efficiency of the photomultiplier tube were made, it was found that the light intensity in the 3450 Å region was lower by a factor of 10 or more from the intensity at 3070 Å. Emissions at other wavelengths corresponding to other OH transitions in the uv were also found to be negligible compared to that at ~ 3070 Å.

Once the OH emissions of the lamp were characterized, several tests were performed in order to insure that OH was the only species detected in this system. In the present study the OH source was H_2O. The photolysis of H_2O has been studied by many investigators, both by steady-state methods and by flash techniques.[10-14] The primary photochemical processes observed in the spectral regions of interest here are:

$$H_2O + h\nu \xrightarrow{\lambda<1850\ \text{Å}} H + OH(X^2\Pi) \tag{3}$$

$$\xrightarrow{\lambda<1365\ \text{Å}} H + OH(A^2\Sigma^+) \tag{4}$$

$$\xrightarrow{\lambda<1236\ \text{Å}} H_2 + O(^1D) . \tag{5}$$

Process (3) appears to be the dominant mode of decomposition at all wavelengths in the region above the LiF cutoff at 1050 Å. In addition, present data suggests that the OH formed from the photolysis of H_2O in its first continuum (~ 1400–1860 Å), is essentially all in its ground vibrational and rotational state.[10,11] Process (4) has been shown to occur at wavelengths less than 1365 Å, but it accounts for only a small fraction of the overall primary process.[12] A pronounced deviation from the Boltzmann distribution of rotational states, with the highest allowed energy levels being significantly populated, has also been noted for Process (4).[13] Evidence for Process (5) was observed in some of the earlier work on the photolysis of H_2O.[14] The O atom formed in Reaction (5) is thought to be in the ^1D state; and hence, the subsequent fast reaction of $O(^1D)$ with H_2O[15,16] would produce two OH radicals.

In the present study, test mixtures consisting of 100 mtorr H_2O and 20 torr of helium were flash photolyzed at wavelengths above 1050 Å. Only when the resonance lamp was turned on was a significant fluorescent signal observed. When this signal was displayed on a multichannel analyzer operated in the multiscaling mode, it appeared as an exponential decay. With the resonance lamp off, the first few channels of the analyzer did show a slight increase in signal above the normal flat baseline signal. This residual signal would appear to be due to excited $OH(A^2\Sigma^+)$, produced by the low wavelength ($\lambda < 1365$ Å) photolysis of H_2O, since this phenomenon was neither observed when all traces of H_2O were removed from the reaction cell nor when H_2O was flash photolyzed with Suprasil quartz or sapphire windows ($\lambda_{Trans} > 1650$ and 1410 Å, respectively). In order to minimize contributions to the observed kinetic decay from flash-produced $OH(^2\Sigma^+)$, an approximate 1 msec delay was employed prior to the initiation of any experimental OH kinetic measurement. Under these conditions the signal from flash produced $OH(^2\Sigma^+)$ was always less than 3% of that resulting from induced resonance fluorescence.

In another series of tests, OH was generated by the uv photolysis of O_3 in the presence of H_2O or H_2. In this case, the $O(^1D)$ from the photolysis of O_3 produced OH via Reactions (6) and (7),

$$O(^1D) + H_2 \rightarrow OH + H \tag{6}$$

$$O(^1D) + H_2O \rightarrow 2OH . \tag{7}$$

For both systems a fluorescence signal similar to that produced from the photolysis of H_2O was observed.

Two additional tests which were initially performed to both insure that OH was the species being detected in this system and that the fluorescence signal generated was directly proportional to the OH concentration, involved systematic variations in the H_2O pressure and flash intensity. In these tests, it was observed that when the H_2O pressure was increased or decreased by a factor of two, the resultant fluorescent signal correspondingly increased or decreased by a factor of two. Similarly, when the flash intensity was varied by a factor of three,

TABLE I. Reaction rate data for the process: OH + CO → CO$_2$ + H.

Temperature (°K)	Helium (torr)	H$_2$O (mtorr)	Co (mtorr)	Flash energy (joules)	K_1 (sec^{-1})	$K_{bimol} \times 10^{13}$ (cc/mol·sec)
220	20	20	0	281	37	
	20	20	20	281	165	1.46
240	20	50	0	88	56	
	20	50	20	88	182	
	20	50	30	88	244	
	20	50	30	281	239	
	20	50	40	88	298	
	20	50	80	88	560	1.49
	100	50	0	88	35	
	100	50	30	88	215	1.49
273	20	100	0	88	78	
	20	100	20	88	180	
	20	100	40	88	292	
	20	100	80	88	510	1.54
298	20	100	0	88	78	
	20	100	20	88	190	
	20	100	40	31	295	
	20	100	40	88	283	
	20	100	40	88[a]	280	
	20	100	40	281	290	
	20	50	40	88	290	
	20	300	40	88	284	
	20	100	60	88	382	
	20	100	80	88	490	1.59
	20(N$_2$)	100	0	281	45	
	20(N$_2$)	100	40	281	250	1.58
373	80	100	0	88	83	
	80	100	15	88	150	
	80	50	40	88	266	
	80	100	40	281	268	
	80	100	60	88	335	
	80	100	60	281	359	
	80	100	80	281	428	1.72

[a]Sapphire window.

the fluorescent signal also changed by a factor of three in the same direction.

In the investigation of Reactions (1) and (2), gas mixtures typically consisted of 20–300 mtorr H$_2$O, 20–100 torr of helium, and either 15–80 mtorr of CO or 40–900 mtorr of CH$_4$. These mixtures were photolyzed utilizing LiF, CaF$_2$, or sapphire windows. In the case of Reaction (2), sapphire was used almost exclusively so as to minimize the photolysis of CH$_4$. Based upon the known absorption spectrum of H$_2$O and previously conducted actinometry on our flash lamp using ethylene as the actinic gas, it was determined that over the spectral region from 1050 to 2000 Å on the order of 0.7 to 7.0 × 10^{11} OH radicals/cm^3 were produced per flash in the reaction cell. (The actual concentration in this range was dictated by the exact flash energy and H$_2$O concentration.) Since the CO and CH$_4$ pressures were adjusted to make Reactions (1) and (2) pseudo-first order with respect to OH, the observed kinetic decays were always exponential. In most cases because of the low signal levels generated from the typically low levels of OH used, multiple flashes were required to produce a smooth kinetic decay curve. However, in order to hold the decomposition of either CO or CH$_4$ through photolysis or reaction to less than 3%, several fillings of the same gas mixture were used for the development of a single experimental decay curve.

In these experiments, where the observed kinetics

were pseudo-first order, the first order rate constants were obtained from a least squares treatment of the slope of the line obtained from a plot of the logarithm of the count rate in each analyzer channel versus time. This treatment was extended out to two and in some cases three 1/e times of the decay. Bimolecular rate constants were obtained from a least squares treatment of the slope of the line obtained from a plot of the pseudo-first order rate constants versus the CO or CH$_4$ pressure. Each bimolecular rate constant value reported in Arrhenius plots 1 and 2 represents, therefore, an average of from 4 to 13 runs, in several cases over widely different experimental conditions.

The gas mixtures used in these experiments were prepared at low pressures (50–3000 mtorr), using an MKS Baratron pressure gauge which was periodically checked against a dibutyl phthalate manometer. The high pressure measurements (10–800 torr) were made with a two-turn Bourdon gauge (Wallace & Tiernan type FA145). The precision to which gas mixtures could be prepared with the exception of H$_2$O, was estimated to be ~3% or better. The H$_2$O pressure could not be metered out as precisely due to adsorption effects within the reaction cell.

The CO used in this experiment was Air Products "high purity" with a stated purity of 99.8%. To remove traces of iron carbonyl, the gas was slowly passed through a U-tube filled with glass beads. The CH$_4$ was Matheson "Gold Label Ultra-high Purity" with a stated purity of 99.995%. The helium was also Matheson "Gold Label Ultra-high Purity" and was used without further purification. The H$_2$O used in all experiments was glass distilled and was degassed using liquid N$_2$ prior to its introduction into the gas handling system.

RESULTS AND DISCUSSION

The results for Reactions (1) and (2) are presented in Tables I and II. Rate constants were measured for both systems over the total pressure range of 20–100 torr of helium. Experiments utilizing 20 torr of N$_2$ were also performed in several cases. When the pseudo-first-order rate constants were adjusted for relative differences in OH diffusion rates for differing total pressures, and diluent gases, the calculated bimolecular rate constants were found to be invariant within the experimental uncertainty for each first-order rate constant ~(±6%). In addition, experiments utilizing variations in H$_2$O pressures over the range from 30–400 mtorr were performed with no experimentally significant deviations being observed. Variations in flash intensity by a factor of 9–10 also resulted in no variations in the bimolecular rate constants. Only in the case of variations in the temperature were changes in the bimolecular rate constants observed outside the experimental uncertainty of the measurements. The data for Reactions (1) and (2) are presented in Arrhenius form in Figs. 1 and 2. Each point on these plots represents an average value of usually between 4–13 individual experiments. The Arrhenius equations obtained from a weighted least squares fit of all the data for Reactions (1) and (2) are

TABLE II. Reaction rate data for the process: OH + CH$_4$ → Products.

Temperature (°K)	Diluent (torr)	H$_2$O (mtorr)	CH$_4$ (mtorr)	Flash energy (joules)	Flash lamp window	K_1 (sec^{-1})	$K_{bimol} \times 10^{15}$ (cc/mol·sec)
240	20(He)	100	0	88	LiF	60	
	20	100	200	88	Sapphire	77	
	20	100	350	281	Sapphire	88	
	20	100	500	88	Sapphire	98	
	20	100	700	281	Sapphire	115	
	20	100	900	88	Sapphire	135	1.85 ± 0.10
	100 (He)	100	0	281	LiF	35	
	100	100	0	281	Sapphire	35	
	100	100	200	281	Sapphire	44	
	100	100	500	281	Sapphire	62	1.85 ± 0.17
276	20(He)	100	0	281	Sapphire	80	
	20	100	175	281	Sapphire	114	
	20	100	350	281	Sapphire	145	
	20	100	700	281	Sapphire	205	4.95 ± 0.25
298	20(He)	100	0	88	LiF	79	
	20	100	150	88	CaF$_2$	114	
	20	100	300	88	CaF$_2$	149	
	20	100	300	88	Sapphire	139	
	20	80	450	88	Sapphire	180	
	20	100	450	88	Sapphire	185	
	20	100	450	88	CaF$_2$	185	
	20	200	450	45	Sapphire	175	
	20	200	450	88	Sapphire	185	
	20	200	450	281	Sapphire	208	
	20	400	450	88	Sapphire	193	
	20	100	600	88	CaF$_2$	225	
	20	200	900	281	Sapphire	310	7.49 ± 0.10
	100(He)	100	0	88	LiF	35	
	100	100	80	88	CaF$_2$	57	
	100	100	150	88	CaF$_2$	69	
	100	100	300	88	CaF$_2$	116	7.5 ± 0.75
	200(N$_2$)	100	0	281	LiF	45	
	20	200	450	281	Sapphire	145	6.9 ± 0.8
373	100(He)	200	0	281	Sapphire	85	
	100	100	40	88	CaF$_2$	110	
	100	100	80	88	CaF$_2$	129	
	100	100	120	281	Sapphire	148	
	100	100	150	88	CaF$_2$	170	
	100	30	180	281	Sapphire	175	
	100	50	180	281	Sapphire	175	
	100	100	180	88	Sapphire	195	
	100	100	180	281	Sapphire	190	
	100	300	180	281	Sapphire	230	
	100	100	250	281	Sapphire	235	
	100	100	350	281	Sapphire	305	23.6

$$k_1 = (2.05 \pm 0.19) \times 10^{-13} \times \exp - [160 \pm 80 \text{ cal mol}^{-1}]/RT$$

$$(220 - 373 \text{ °K})$$

and

$$k_2 = (2.36 \pm 0.21) \times 10^{-12} \times \exp - [3400 \pm 175 \text{ cal mol}^{-1}]/RT$$

$$(240 - 373 \text{ °K}) .$$

Units for both expressions are cm^3 mol^{-1}·sec^{-1}. The error limits in these expressions were determined by the goodness of fit of the least squares straight line to the individual data points and represents the probable er-

ror within the given experimental temperature ranges. An examination of the uncertainties in the rate constants for these reactions outside of the experimental temperature range, determined by drawing maximum and minimum slopes through the designated error bars, indicates that the maximum estimated uncertainties for Reaction (1) could be ±0.80×10^{-13} and ±130 cal mol^{-1} in A and E, respectively. For Reaction (2), the values could be ±1.02×10^{-12} and ±300 cal mol^{-1} for A and E, respectively.

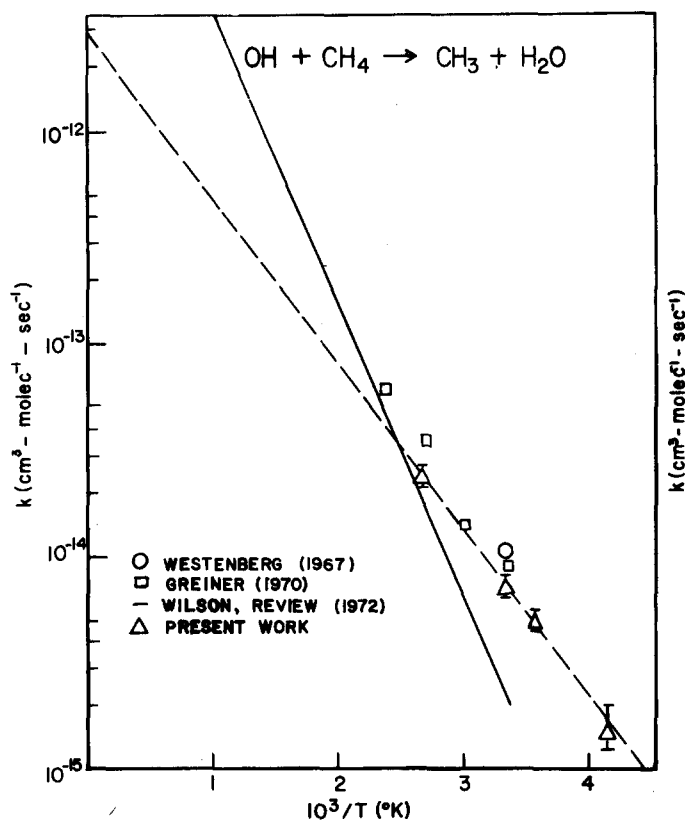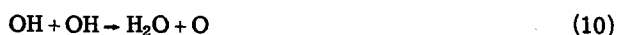In the reported study, wide variation in experimental

FIG. 2. An Arrhenius plot showing the temperature dependence of the reaction of OH with CH_4.

conditions were carried out in an effort to show that kinetic complications were not effecting the observed rate constants. These complications could have resulted from having excessive concentrations of other radical species. Another possibility might involve the reaction or deactivation of vibrationally and/or rotationally excited OH.

The principal secondary OH reactions which require consideration here are,

$$OH + OH + M \rightarrow H_2O_2 + M \qquad (8)$$

$$OH + H + M \rightarrow H_2O + M \qquad (9)$$

$$OH + OH \rightarrow H_2O + O \qquad (10)$$

$$O + OH \rightarrow O_2 + H \qquad (11)$$

$$OH + CH_3 \rightarrow CH_2 + H_2O . \qquad (12)$$

In each of the above processes, it is seen that the rate of disappearance of OH depends on the square power of the radical concentration; and hence, on the square power of the flash intensity. These reactions, if important, should therefore result in a significant dependence of k_1 or k_2 on flash intensity. In the case of Reactions (8) and (9), it would appear that they would only become important at low temperatures and high total pressures. In fact, calculations based upon existing data[17-20] for these two reactions suggest that these particular secondary reactions should not be important under the experimental conditions employed in this study. Even so, a set of tests were carried out in which the total pres-

sure was varied by a factor of 5 at 240 °K, and the flash intensity was varied by a factor of 3. The results (see Tables I and II) show that the observed rate constants were invariant within the experimental uncertainty of the measurements.

Reactions (10), (11), and (12) would be expected to be of possible significance at both low and moderate temperatures. At 373 °K, tests were performed in which the initial OH concentration was varied by a factor of 6 via variations in the H_2O pressure by a factor of 2 and by variations in the light intensity by a factor of 3. In no case was there a variation in the observed rate constant outside of the previously indicated experimental uncertainties.

In another series of experiments performed on both the CO and CH_4 systems, the number of consecutive flashes per filling for a particular gas mixture was also varied. In all tests involving the reactant CO, it was found that variations in the number of flashes per filling over the range of 20 to 100 gave near identical values for the pseudo-first-order rate constant with a LiF window mounted on the flash lamp. In similar test involving CH_4, a sapphire window was used on the flash lamp to prevent photolysis of the methane below 1400 Å. In this system, a variation in the number of flashes per gas filling in the range of 10–50 flashes per filling again showed no variation in the experimentally observed pseudo-first-order rate constant. The above tests would seem to rule out, therefore, possible interference resulting from stable product formation.

As indicated earlier, a final source of systematic error in these measurements could involve rotationally or vibrationally excited OH species. Although the previously mentioned tests, involving 3070 and 3450 Å filters being placed over the resonance lamp, indicated that vibrationally excited OH was not detected directly by the system, the question of initially produced excited OH relaxing to the $\nu'' = 0$ level remained unanswered. If this were occurring, the slow production of detectable ground state OH would cause an apparent decrease in the observed pseudo-first-order rate constant. To test for the presence of this quenching process, experiments were performed utilizing gas mixtures containing 40 mtorr of CO, 20 torr of helium and H_2O pressures varying over a factor of 6. In addition, experiments at 100 torr of helium and 20 torr of N_2 were performed. In no case was the experimentally determined rate constant outside of the range of the experimental error. Similar tests carried out on mixtures containing CH_4, utilizing both helium and N_2 as diluents, again resulted in rate constants which were invariant. The possibility that at the highest pressures of CH_4 employed in this study quenching by CH_4 might become significant was also considered. However, the fact that all plots of the pseudo-first-order rate constant versus CH_4 pressure were linear within the experimental error would tend to discount this possibility. It was concluded from the above test that rotationally and/or vibrationally excited OH species were unimportant in defining the values of the bimolecular rate constants, k_1 and k_2.

COMPARISON WITH PREVIOUS RESULTS

$CO + OH \rightarrow CO_2 + H$

There have been several recent measurements of the rate constant for Reaction (1). Westenberg and deHaas[5] examined Reaction (1) over a temperature range of 298° to 915 °K using a fast flow reactor with ESR detection. The OH radical in this study was generated by injecting NO_2 into a stream of H atoms. Within their expressed experimental uncertainty, their data when expressed in Arrhenius form was nonlinear over the above temperature range. These authors suggested that such nonlinear Arrhenius behavior could be explained by assuming a nonlinear transition state species of the type
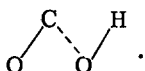
Using transition state theory and taking the vibrational modes for the above complex to be analogous to that of the HONO molecule, they were able to fit their data to a curve where the experimental activation energy was zero.

At 300 °K, a comparison of our data with that of Westenberg and deHaas shows our data to be ~ 16% higher. The two values, however, certainly do agree within the expressed experimental uncertainties of the two studies. Concerning the temperature dependence observed for the reaction in the two studies, within the experimental error bars of the data reported in this study, no curvature in the Arrhenius plot can be justified. However, the smaller temperature range covered in this study compared to the above authors' may be significant.

In another recent study of Reaction (1) by Niki and Stuhl,[21] a resonance fluorescence technique was employed in making rate measurements at 300 °K. Their value of 1.35×10^{-13} cm^3 mol$^{-1} \cdot$ sec^{-1} is in good agreement with the value measured in this study within the assigned experimental uncertainties.

In a recent review article by Wilson,[4] all rate data on Reaction (1) prior to 1972 was evaluated. In this evaluation, an attempt was made to fit both the high and low temperature data to a common Arrhenius expression (see Fig. 1):

$$k_{CO} = 5.1 \times 10^{-13} \exp(-600/RT) \text{ cm}^3 \text{ mol}^{-1} \cdot \text{sec}^{-1}.$$

This rate expression gives k values which are too high compared to this work at temperatures above ~ 250 °K. The stronger temperature dependence indicated in the above expression would seem to be due to Wilson[4] giving a heavy weighting factor to the high temperature data. One earlier study reviewed by Wilson[4] but given little weight in defining the above Arrhenius expression was the work by Greiner[22] over the temperature range of 300°–500 °K (see Fig. 1). The technique used in this investigation was that of flash photolysis-kinetic absorption spectroscopy. The results obtained are in very good agreement with those reported here both at 300 °K (1.42×10^{-13} vs 1.58×10^{-13}) and at higher temperatures. The activation energy measured by Greiner,[21] 230 cal^{-1}

$\cdot$ mol^{-1} is also in good agreement with that measured in this work.

Finally, as this study was being finished, it was learned that another study had also been completed on this same system by Smith and Zellner.[23] The technique used by these investigators was flash photolysis-resonance absorption spectroscopy. Their room temperature value of 1.45×10^{-13} cm^3 mol$^{-1} \cdot$ sec^{-1} again shows good agreement with the value measured here. Over the temperature range of 210 to 460 °K, a slight positive temperature dependence was indicated which Smith and Zellner believed showed some curvature at the high temperature end. This curvature if real, however, was very slight and within the experimental uncertainty of both measurements. The agreement on temperature dependence is quite good.

$CH_4 + OH \rightarrow CH_3 + H_2O$

One of the early direct measurements of k_2 was that by Wilson and Westenberg.[24] In this study, OH was generated in a flow system by titrating H atoms with NO_2, $H + NO_2 \rightarrow OH + NO$. The change in the OH concentration with added CH_4 was then determined using ESR detection of the OH. These authors measured k_2 at only one temperature, 300 °K, and obtained a value for k_2 of 1.08×10^{-14} cm^3 mol$^{-1} \cdot$ sec^{-1}. This value is in reasonably good agreement ($\pm 25\%$) with our measured value of k_2.

A more extensive study by Horne and Norrish[25] covered the temperature range of 300° to 425 °K. These authors used the flash photolysis of H_2O as their source of OH, and then followed the kinetic decay of OH by absorption spectroscopy. Their 300 °K value of k_2 is nearly a factor of two higher than that reported in this work, but it is perhaps significant that Horne and Norrish were required to work with concentrations of OH in excess of 10^{-14} radicals/cm^3. Under these conditions, the CH_3 product from Reaction (2) would probably react rapidly with a second OH radical thus producing a stoichiometric correction factor of two. Dividing these authors' value of k_2 by two thus brings it into excellent agreement with this work as well as several other investigators. The activation energy calculated from the data of Horne and Norrish[25] is ~ 5.0 kcal/mole and is considerably higher than that measured in this work, 3.4 kcal/mole. Although it is difficult to show quantitatively at this time, it is believed that the stronger temperature dependence observed by Horne and Norrish[25] was the result of complex secondary reactions. For example, it is quite possible that at the higher OH concentrations used in their study the stoichiometric factor itself might have been significantly temperature dependent.

One of the most recent studies of Reaction (2) was that carried out by Greiner.[26] This investigator covered the temperature range of 300 –500 °K and again used the technique of flash photolysis-kinetic absorption spectroscopy. However, a major difference between the work of Greiner[26] and that by Horne and Norrish[24] was the much lower concentrations of OH employed by the former investigator, ~ 3×10^{13} versus ~ 3×10^{14} cm^{-3}. The probability of significant secondary reactions oc-

curring in Greiner's study was thus considerably reduced. Over the temperature range of 300 to 500 °K, Greiner[26] reported an activation energy of ~ 3.4 kcal/mole and a 300 °K value of k_2 of 8.8×10^{-15} cm^3 mol^{-1} · sec^{-1}. Both the activation energy and the 300 °K results are in excellent agreement (±10%) with that measured in this study. It should be noted also that the present study was carried out using an OH concentration nearly two orders of magnitude lower than that employed by Greiner.[26]

In his critical review of OH rate data, Wilson[4] recommended the Arrhenius expression:

$$k = 4.7 \times 10^{-11} \exp(-2500/T) .$$

It was pointed out by Wilson[4] that Greiner's[26] data were deemphasized due to the fact that they did not extrapolate into the available high temperature data. The argument was also presented that Greiner's results could have been in error due to the formation of significant quantities of H$_2$O$_2$. In the present study, however, where much lower OH concentrations were employed and the number of flashes per filling could be varied, it has been clearly demonstrated that H$_2$O$_2$ formation was not important. It is to be expected, therefore, that Greiner's[26] results were also free of secondary reactions.

CONCLUSIONS

(i) We have reported some of the first measurements of k_1 and k_2 at temperatures below 300 °K. The rate constant expressions over nearly 150 deg are:

$$k_1 = (2.15 \pm 0.19) \times 10^{13} \exp -[160 \pm 80 \text{ cal mol}^{-1}]/RT$$

and

$$k_2 = (2.36 \pm 0.21) \times 10^{-12} \exp -[3400 \pm 175 \text{ cal mol}^{-1}]/RT$$

Units are in cm^3 mol^{-1} · sec^{-1}.

(ii) Our results for Reaction (1) would indicate a discrepancy between the high temperature flame data and our extrapolated Arrhenius line of slightly over a factor of two. For Reaction (2), this discrepancy at flame temperatures would be somewhat greater than one order of magnitude.

(iii) Although it has been suggested by some investigators[5,23] that the discrepancy between the low and high temperature data for Reaction (1) is evidence of nonlinear Arrhenius behavior, serious doubt still remains. There are now at least three OH reaction systems where such discrepancies have been observed.

$$OH + CO \rightarrow CO_2 + H$$

$$OH + H_2 \rightarrow H_2O + H$$

$$OH + CH_4 \rightarrow CH_3 + H_2O .$$
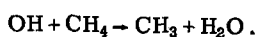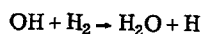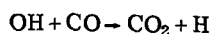
Considering the complexities of those experiments which have been carried out at very high temperatures, it is not at all unlikely that some if not all of the disagreement between the low and high temperature data could be the result of large uncorrected systematic errors.

(iv) Extensive direct measurements of each of the rate constants for the above systems are now needed in the temperature range of 400 −1500 °K to resolve this very important question.

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[1] Symposium on Sources, Sinks, and Concentrations of Carbon Monoxide and Methane in Earth's Environment, a joint meeting held at St. Petersburg, Florida, 15–17 Aug. 1972.
[2] H. Levy II, J. Geophys. Res., 78, 5325 (1973).
[3] R. M. Fristrom and A. A. Westenberg, Flame Structure (McGraw-Hill, New York, 1965).
[4] W. E. Wilson, Jr., J. Phys. Chem. Ref. Data, 1, 535 (1972).
[5] A. A. Westenberg and N. deHaas, J. Chem. Phys. 58, 4061 (1973).
[6] N. R. Greiner, J. Chem. Phys. 51, 5049 (1969).
[7] D. D. Davis and R. B. Klemm, Int. J. Chem. Kinetics 4, 367 (1972).
[8] D. D. Davis, R. E. Huie, J. T. Herron, M. Kurylo, and W. Braun, J. Chem. Phys. 56, 4868 (1972).
[9] R. D. Davis and W. Braun, Appl. Opt. 7, 2071 (1968).
[10] G. Black and G. Porter, Proc. R. Soc. A 266, 185 (1962).
[11] K. H. Welge and F. Stuhl, J. Chem. Phys. 46, 2440 (1967).
[12] T. Carrington, J. Chem. Phys. 41, 2012 (1964).
[13] M. Kaneko, Y. Mori, and I. Tanaka, J. Chem. Phys. 48, 4468 (1968).
[14] L. J. Stief, J. Chem. Phys. 44, 277 (1966).
[15] R. F. Heidner III, D. Husain, and J. R. Wiesenfeld, Chem. Phys. Lett. 16, 530 (1972).
[16] C. J. Fortin, D. R. Snelling, and A. Tardif, Can. J. Chem. 50, 2747 (1972).
[17] J. Caldwell and R. A. Back, Trans. Faraday Soc. 61, 1939 (1965).
[18] J. B. Homer and I. R. Hurle, Proc. R. Soc. 314, 585 (1970).
[19] A. A. Westenberg and N. deHaas, J. Chem. Phys. 58, 4066 (1973).
[20] J. E. Breen and G. P. Glass, J. Chem. Phys. 52, 1082 (1970).
[21] F. Stuhl and H. Niki, J. Chem. Phys. 57, 3671 (1972).
[22] N. R. Greiner, J. Chem. Phys. 51, 5049 (1969).
[23] R. Zellner and I. Smith, J. Chem. Soc., Faraday Trans. II 69, 1617 (1973).
[24] W. E. Wilson and A. A. Westenberg, Eleventh Symposium (International) on Combustion, Berkeley, CA, 1966 (Combustion Institute, Pittsburgh, 1967), p. 1143.
[25] D. G. Horne and R. G. W. Norrish, Nature 215, 1373 (1967).
[26] N. R. Greiner, J. Chem. Phys. 53, 1070 (1970).