

A Flash Photolysis-Resonance Fluorescence Study of the Reaction of Atomic Hydrogen with Molecular Oxygen $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$

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Abstract

Using the technique of flash photolysis-resonance fluorescence, absolute rate constants have been measured for the reaction $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ over a temperature range of 220–360°K. Over this temperature range, the data could be fit to an Arrhenius expression of the following form:

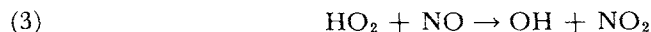
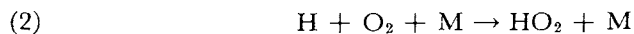
$$k_{\text{Ar}} = (6.75 \pm 1.1) \times 10^{-33} \exp [685 \pm 128 \text{ cal/mole}]/RT$$

The units for k_{Ar} are $\text{cm}^6/\text{mole}\cdot\text{s}$. At 300°K the relative efficiencies for the third-body gases Ar:He:H₂:N₂:CH₄ were found to be 1.0:0.93:3.0:2.8:22. Wide variations in the photoflash intensity at several temperatures demonstrated that the reported rate constants were measured in the absence of other complex chemical processes.

Introduction

The reaction of atomic hydrogen with molecular oxygen in the presence of a third body M has long been recognized as one of the important chain-terminating steps at the second explosion limit of the hydrogen-oxygen system. Because of its importance in this system, the reaction of H with O₂ has been the subject of numerous high-temperature shock tube and flame studies, most of which have been reviewed by Baulch et al. [1].

More recently this reaction has received considerable attention due to its importance in atmospheric chemical dynamics. Based on recent rate measurements of the reaction of HO₂ with NO [3], a chain reaction sequence involving the species H, OH, and HO₂ would appear to be of considerable importance in both the troposphere and stratosphere, for example,



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Thus the net result of this chain would be the conversion of CO to CO₂ and NO to NO₂. (The later process is now believed to be of considerable importance in the promotion of photochemical smog.) Since temperatures in the troposphere and stratosphere cover a range of $\sim 215\text{--}300^\circ\text{K}$, rate data for reaction (2) extrapolated from previous high-temperature studies could contain large uncertainties. To date, only one study of this reaction at temperatures below 293°K has been reported in the literature [3]. This study, however, was carried out in a flow system, where wall reactions could have possibly influenced the results.

In addition to the above considerations, reaction (2) is also of intrinsic theoretical interest as an example of yet another third-order reaction which is sensitive to the type of deactivating third body M. Quantitative data on the efficiencies of various third bodies is now needed in order to develop more refined theories for treating three-body recombination reactions.

For the above reasons we have undertaken a detailed study of reaction (2) over a wide range of experimental conditions. Most important among these were a temperature range of $360\text{--}220^\circ\text{K}$, a pressure range of 10–500 torr, and the use of the third-body species He, Ar, N₂, H₂, and CH₄. The experimental technique employed was that of flash photolysis-resonance fluorescence. Of considerable importance in this study is the fact that all experiments were carried out in a static reaction vessel where the volume of gas being sampled was small compared to the total volume of the cell. Since sampling times were also kept short (5 ms or less), any possible effect on the kinetic decays due to wall reactions was rendered unimportant.

Experimental

The flash photolysis-resonance fluorescence system has been previously described [4,5] and will be discussed only briefly here. In this study, H atoms were generated from the vacuum ultraviolet flash photolysis of CH₄. In a typical experiment, a mixture of methane, molecular oxygen, and a diluent gas was flash photolyzed, producing approximately 10^{11} H atoms per cm³. A small fraction of these H atoms was then excited by absorbing Lyman- α radiation (1216 \AA) from a continuously operated hydrogen resonance lamp. The resonance lamp used in this study was of the flow type described by Davis and Braun [6] and utilized Matheson ultra-high-purity He as the flow gas. Decomposition of very small traces of H₂O in the He was the source of the Lyman- α radiation. Since in this experiment atomic oxygen was also produced from the flash photolysis of O₂, it was necessary to filter out any oxygen resonance radiation from the hydrogen lamp. In this case, advantage was taken of the fact that molecular oxygen has a window at Lyman- α ($\epsilon \approx 0.25\text{ cm}^{-1}\text{ atm}^{-1}$), and an oxygen filter chamber was installed between the resonance lamp and the reaction cell. The amount of oxygen in the filter chamber was determined experimentally in our system to be ≈ 150 torr. This reduced the transmission of the oxygen resonance lines by approximately a factor of 100 and that of the Lyman- α line by ≈ 1.2 .

In addition to removing any oxygen resonance radiation from the hydrogen lamp, and hence, eliminating any possible signal from O atoms, the molecular oxygen filter also prevented any significant CW photolysis of the reactant gas mixture. Under these experimental conditions all impurity lines at $\lambda > 1216 \text{ \AA}$ but $< 1700 \text{ \AA}$ would have been removed. This point will be expanded on later in the text.

The decay of atomic H in the gas mixture was monitored by following the Lyman- α fluorescence from excited H atoms. Using pulse-counting techniques, the fluorescence signal was amplified and then recorded on a multichannel analyzer. A typical decay curve is shown in Figure 1. (The time base per channel is $107 \mu\text{s}$.) Since the number of counts per flash was small, and hence, subject to statistical variations, the experiment was performed several times with each filling of the gas mixture. To avoid any accumulation of products which might complicate the reaction, the gas mixture was normally changed after 30–40 flashes. In most experiments several gas fillings were used to acquire between 500 and 1000 counts in the first effective channel of the kinetic decay.

In this system where the O_2 and M concentrations were in large excess over the H atom concentration pseudo first-order conditions were maintained throughout the H atom decay. Thus a plot of the logarithm of the count rate, after correction for the resonance lamp background, against time produced a straight line having a slope equal to the pseudo first-order rate constant k_1 . By varying the (O_2) concentration at a fixed total pressure, the slope of a plot of k_1 versus (O_2) gave the pseudo second-order rate constant k_2 (see Fig. 2). Finally, the third-order rate constant was obtained by either dividing the second-order rate constant by a specific total pressure or from the slope of a plot of k_2 versus (M) (see Fig. 3). For the third bodies N_2 and Ar both processes were used; whereas, for He, H_2 , and CH_4 only the first method was employed since only one pressure was examined in each case.

In the determination of the third-order rate constant from the slope of the plot of k_2 versus total pressure, a nonzero intercept was observed in all cases. A comparison of the third-order rate constant derived from the above method to that obtained by dividing the bimolecular rate constant by a particular total pressure always showed the largest deviation at low total pressures. This suggested that methane could also be serving as an important third body in the low-pressure experiments. A set of experiments was carried out, therefore, in which the methane concentration was varied at a constant O_2 concentration and total pressure. The third-order rate constant k_{CH_4} was determined from the slope of a plot of k_2 versus (CH_4) divided by (O_2) (M). An example of the correction resulting from the third body effect of methane is presented in Table I. (For temperatures of 220, 260, and 360°K , the correction for $\text{M} = \text{CH}_4$ was calculated assuming the same relative efficiencies as for the gases CH_4 , N_2 , and Ar as measured at 298°K .) A plot of k_{bi} versus total pressure, after the correction for methane, is presented in Figure 4.

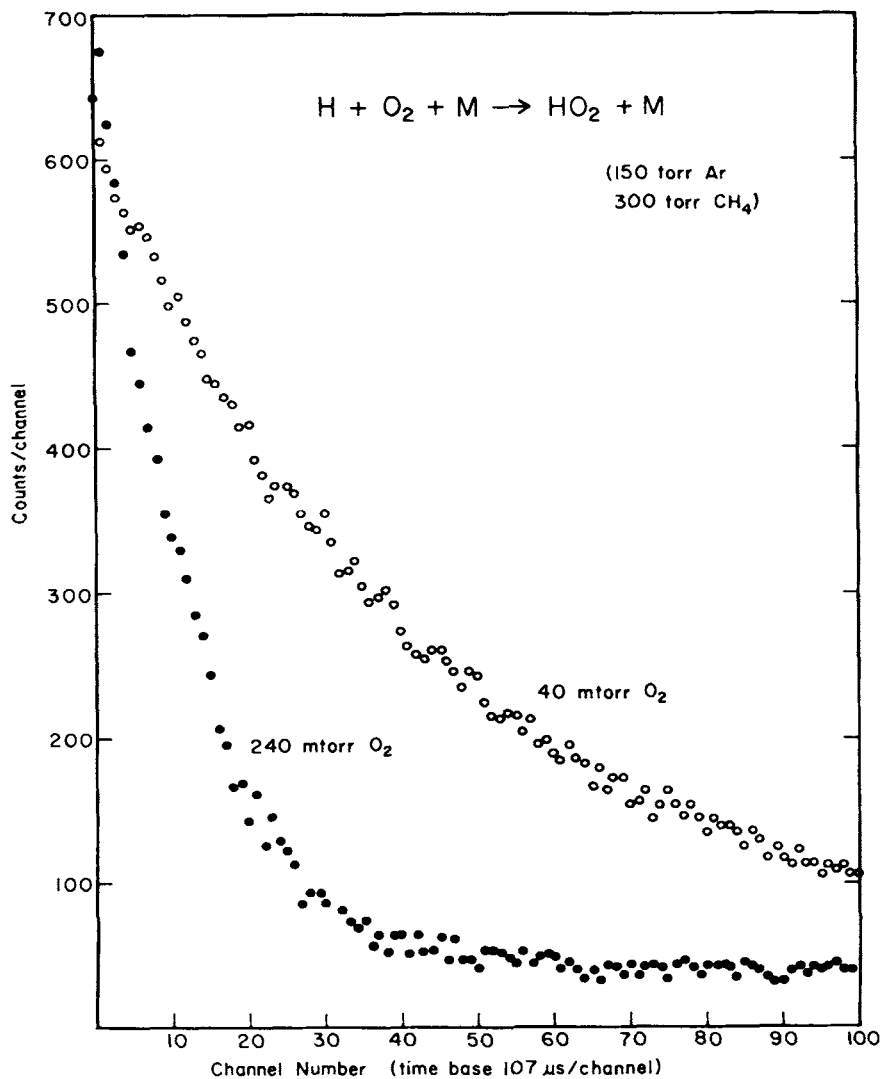
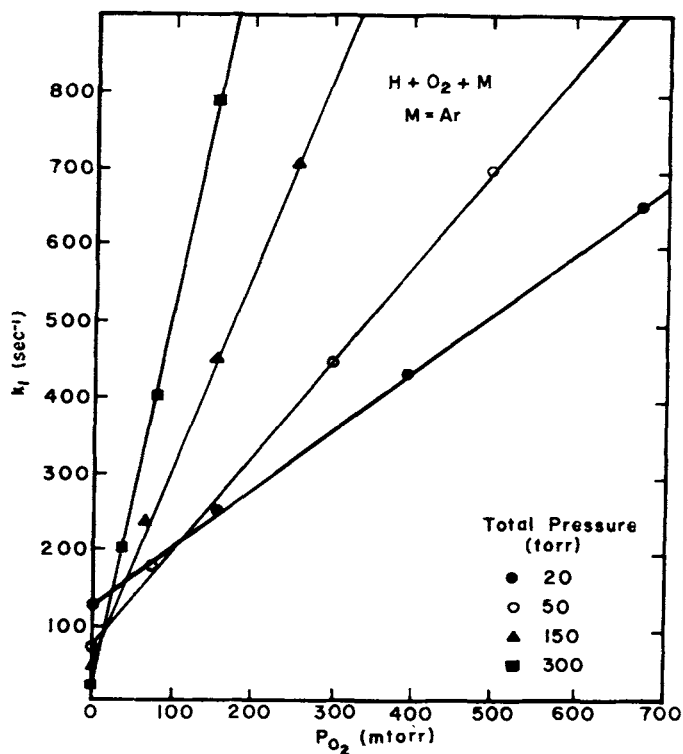


Figure 1. Kinetic decay curves for reaction of atomic hydrogen with molecular oxygen.

The uncertainty in determining the first-order rate constant was typically 3–4%. It has been previously shown [4,5] that this uncertainty is due almost entirely to the combined uncertainty generated from multiple gas pressure measurements. The error limits on the second-order rate constants were derived from drawing maximum and minimum slopes through the error bars on the k_1 plotted against the (O_2) . These plots were similar to those shown in Figure 2;

Figure 2. Plot of first-order rate constant vs. O_2 pressure.TABLE I. Rate measurements on the reaction $\text{H} + \text{O}_2 + \text{Ar} \rightarrow \text{HO}_2 + \text{Ar}$ at 298°K .

Total Pressure torr M = Ar	$k_{\text{Ar}} \times 10^{32}$ $\text{cm}^6 \text{molec}^{-2} \text{s}^{-1}$	% of Correction for M = CH_4	$k_{\text{Ar}} \times 10^{32}$ $\text{cm}^6 \text{molec}^{-2} \text{s}^{-1}$ after correction
20	3.02	32%	2.04 ± 0.23
50	2.44	13%	2.12 ± 0.20
150	2.11	4%	2.02 ± 0.10
300	2.01	<1%	2.01 ± 0.13

Corrections are due to the reaction $\text{H} + \text{O}_2 + \text{CH}_4 \rightarrow \text{HO}_2 + \text{CH}_4$.

^a Calculated from the equation $k_{\text{Ar}} = k_{\text{bi}}/[\text{M}]$.

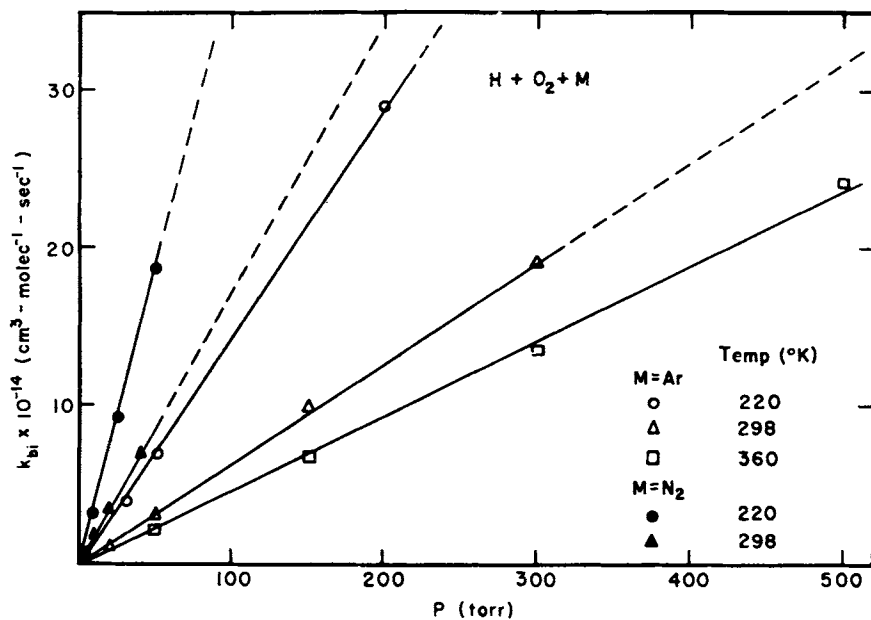
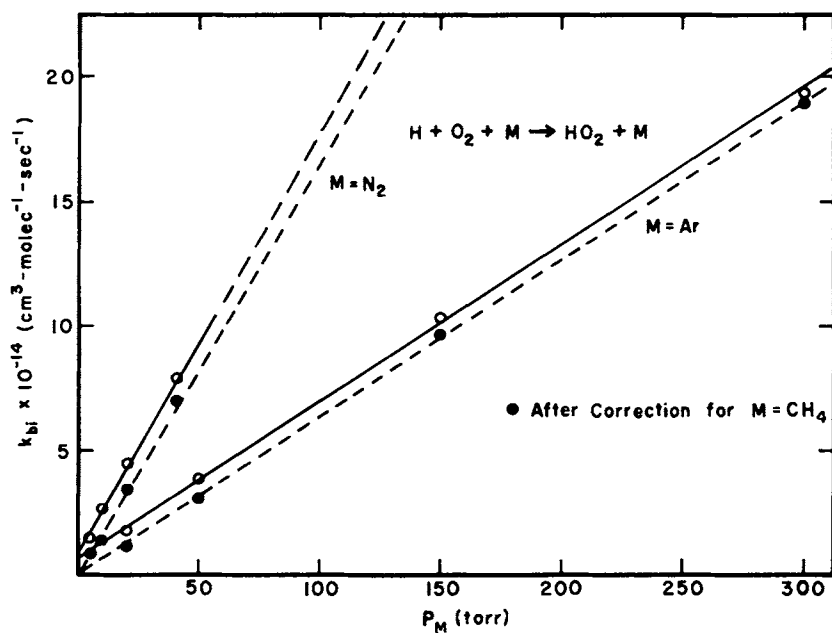


Figure 3. Plot of second-order rate constant vs. total pressure.

Figure 4. Plot of second-order rate constant vs. total pressure, corrected for the effect of CH_4 .

however, the scales on the ordinate and abscissa were adjusted for each pressure to facilitate the drawing of maximum and minimum slopes through vertical error bars. (It has been previously established that the uncertainty in the abscissa (O_2 pressure) is small compared to that in the ordinate (pseudo first-order rate constant). The uncertainty in the third-order rate constants was arrived at in a manner similar to that described above for the pseudo second-order rate constant. For the third-order case, maximum and minimum slopes were drawn through the error bars of a plot of k_2 versus total pressure. The error bars placed on k_2 were those derived from the maximum and minimum slope technique. In general, the uncertainties for the second- and third-order rate constants were determined to be 5–10% and 10–15%, respectively. (The 10–15% uncertainty figure quoted above is for that case where k_{Ar} and k_{N_2} were determined from a plot of k_2 versus $[\text{M}]$.) The best straight-line fit to the data in each of the first-, second- and third-order plots was established using a least square computer program, and in every case the uncertainties in the k values derived from this treatment were well within the error limits determined from the maximum and minimum slope technique. The final uncertainty in the Arrhenius rate expression was again derived from a consideration of the maximum and minimum slopes that could be drawn through the error bars of a plot of k_{Ar} versus $1/T$ (see Fig. 5).

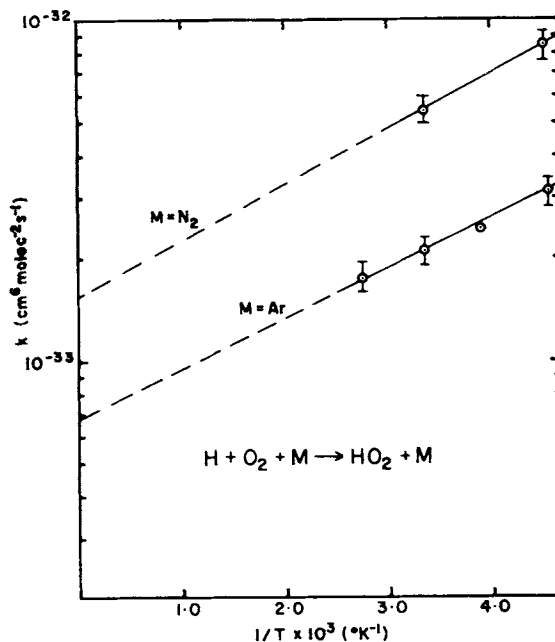


Figure 5. Arrhenius plot of third-order rate constant for reaction of atomic hydrogen with O_2 .

A more complete discussion of both systematic and random errors involved with the flash photolysis-resonance fluorescence technique can be found in earlier papers from this laboratory [4,5].

The gases N₂, He, Ar used in this study were Matheson Gold Label (99.999% claimed purity), and all were used in experiments without further purification. The methane, also Matheson Gold Label, was degassed briefly several times at liquid nitrogen temperature. High-pressure gas measurements (8–500 torr) were made on a two-turn Wallace and Tiernan Bourdon type gauge. Low-pressure measurements (<5 torr) were carried out on a Granville-Phillips capacitance manometer which was calibrated against a dibutyl phthalate manometer. All gas mixtures were allowed to equilibrate at room temperature in storage bulbs for 30–45 min before initiating actual experiments. As indicated above, it has been previously demonstrated that in this system the total uncertainty in the first-order rate constant due to the multiple pressure measurements was on the order of 3–4%.

Results and Discussion

All data collected at room temperature are presented in Table II. Those data collected at temperatures other than room temperature are given in Table III. At room temperature (298°K) the third-order rate constants for the reaction $H + O_2 + M$ were found to be as follows:

$$\begin{aligned} (2.02 \pm 0.23) \times 10^{-32} \text{ cm}^6/\text{mole}^2\text{-s with } M = \text{Ar} \\ (1.88 \pm 0.19) \times 10^{-32} \text{ cm}^6/\text{mole}^2\text{-s with } M = \text{He} \\ (5.90 \pm 1.18) \times 10^{-32} \text{ cm}^6/\text{mole}^2\text{-s with } M = \text{H}_2 \\ (5.46 \pm 0.70) \times 10^{-32} \text{ cm}^6/\text{mole}^2\text{-s with } M = \text{N}_2 \\ (4.20 \pm 1.83) \times 10^{-31} \text{ cm}^6/\text{mole}^2\text{-s with } M = \text{CH}_4 \end{aligned}$$

This established the relative efficiency of the third bodies Ar:He:H₂:N₂:CH₄ as 1.0:0.93:3.0:2.8:22.

Due to the high quenching efficiency of the Lyman- α fluorescence signal by both N₂ and H₂, most of the temperature-dependence experiments were carried out using only the one diluent gas, Ar. The temperature study was performed over the range 220–360°K and over a pressure range of 10–500 torr (see Fig. 3). An Arrhenius plot showing the temperature dependence of the third-order rate constant k_{Ar} is shown in Figure 5. The data presented in this figure could be fit to a simple straight line over the indicated temperature range and resulted in the expression

$$k_{Ar} = (6.75 \pm 1.1) \times 10^{-33} \exp (685 \pm 128 \text{ cal/mole})/RT$$

The error limits in the above expression were determined as described earlier, from a consideration of the maximum and minimum slopes that could be drawn through the error bars on each k_{Ar} value.

TABLE II. Rate measurements on the reaction $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ at 298°K.

M	Total Pressure (torr)	Methane (mtorr)	Oxygen (mtorr)	Flash Energy (J)	First Order Rate Constant ^a k_1 (s^{-1})	Third Order Rate Constant ^a $\times 10^{12}$ ($\text{cm}^3\text{-molec}^{-2}\text{-s}^{-1}$)
Ar	50	300	--	88	60.2 \pm 1.24	
	50	300	500	88	645 \pm 25.8	
	50	300	300	88	416 \pm 16.6	
	50	300	80	88	170 \pm 6.8	2.23 \pm 0.24
	50	300	--	51	60 \pm 2.4	
	50	300	80	51	181 \pm 7.2	
	50	300	80	51	189 \pm 7.6	
	50	300	300	51	440 \pm 17.6	
	50	300	300	51	476 \pm 19.0	
	50	300	500	51	690 \pm 27.6	
	50	300	500	51	699 \pm 28.0	2.12 \pm 0.20
	50	300	500	26	645 \pm 25.7	
	50	300	300	26	430 \pm 17.2	
	50	300	80	26	187 \pm 7.5	2.26 \pm 0.28
	50	300	300	11	435 \pm 17.4	
	50	300	80	11	177 \pm 7.1	2.14 \pm 0.20
	20	300	--	51	120 \pm 4.8	
	20	300	150	51	238 \pm 9.5	
	20	300	450	51	400 \pm 16.0	
	20	300	900	51	690 \pm 27.6	2.04 \pm 0.23
Ar	150	300	--	51	41.6 \pm 1.7	
	150	300	40	51	220 \pm 8.8	
	150	300	120	51	476 \pm 19.0	
	150	300	240	51	855 \pm 34.2	2.02 \pm 0.10
	300	300	--	51	47.6 \pm 1.9	
	300	300	20	51	195 \pm 7.8	
	300	300	60	51	430 \pm 17.2	
	300	300	120	51	282 \pm 31.3	2.01 \pm 0.13
	30	200	--	51	88 \pm 3.5	
	20	200	40	51	180 \pm 7.2	
	20	200	120	51	280 \pm 11.2	
	20	200	240	51	430 \pm 17.2	5.51 \pm 0.77
	40	200	--	51	71 \pm 2.8	
	40	200	20	51	137 \pm 5.5	
H ₂	40	200	60	51	225 \pm 9.0	
	40	200	120	51	370 \pm 14.8	5.54 \pm 0.52
	5	100	--	51	190 \pm 7.6	
	5	100	80	51	250 \pm 10.0	
	5	100	240	51	334 \pm 13.4	
	5	100	480	51	440 \pm 17.6	5.48 \pm 0.94
	10	200	--	51	139 \pm 5.6	
	10	200	60	51	220 \pm 8.8	
	10	200	180	51	317 \pm 12.7	
	10	200	360	51	470 \pm 18.8	5.0 \pm 0.68
	50	300	--	88	85 \pm 3.4	
	50	300	--	51	80 \pm 3.2	
	50	300	80	88	187 \pm 7.5	
	50	300	80	51	182 \pm 7.3	
He	50	300	200	51	345 \pm 13.8	
	50	300	300	51	449 \pm 18.0	
	50	300	300	88	445 \pm 17.8	
	50	300	400	51	540 \pm 21.6	
	50	300	500	88	667 \pm 26.7	
	50	300	500	51	685 \pm 27.4	
	50	300	500	51	680 \pm 27.2	\pm .19
	20	200	--	88	160 \pm 6.4	
	20	200	20	88	215 \pm 8.6	
	20	200	50	88	250 \pm 10.0	
CH ₄	20	200	100	88	317 \pm 12.7	5.90 \pm 1.18
	20 (Ar)	50	200	51	230 \pm 9.2	
	20 (Ar)	100	200	51	235 \pm 9.4	
	20 (Ar)	300	200	51	252 \pm 10.1	
	20 (Ar)	600	200	51	278 \pm 11.1	42.4 \pm 18.30

^a All reported third-order rate constants have been corrected for the contribution made by the reaction $\text{H} + \text{O}_2 + \text{CH}_4 \rightarrow \text{HO}_2 + \text{CH}_4$.

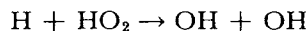
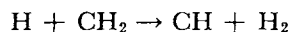
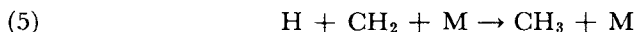
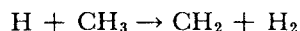
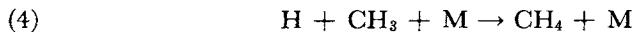
TABLE III. Temperature dependence of rate measurements on the reaction $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$.

M	T (°K)	Total Pressure (torr)	Methane (mtorr)	Oxygen (mtorr)	Flash Energy (J)	First Order Rate Constant k (s ⁻¹)	Third Order Rate Constant ^a × 10 ³² (cm ⁶ molec ⁻² s ⁻¹)
Ar	360	50	200	--	51	85.6 ± 3.4	
		50	200	75	51	156 ± 6.2	
		50	200	250	51	270 ± 10.8	
		50	200	500	51	427 ± 17.1	1.76 ± 0.16
		150	200	--	51	47.6 ± 1.9	
		150	200	50	51	148 ± 5.9	
		150	200	200	51	426 ± 17.0	
		150	200	400	51	855 ± 34.2	1.81 ± 0.13
		150	200	--	88	51.3 ± 2.1	
		150	200	75	88	217 ± 8.68	
		150	200	250	88	535 ± 21.4	
		150	200	500	88	833 ± 33.32	1.78 ± 0.15
		150	200	--	11	48.5 ± 1.9	
		150	200	75	11	220 ± 8.8	
		150	200	250	11	555 ± 22.2	1.75 ± 0.13
		500	200	--	51	30 ± 1.2	
		500	200	20	51	242 ± 9.6	
		500	200	80	51	625 ± 25.0	
		500	200	160	51	1175 ± 47.0	1.80 ± 0.14
Ar	260	50	200	--	51	48.7 ± 1.9	
		50	200	75	51	191 ± 7.6	
		50	200	250	51	500 ± 20.0	
M		50	200	500	51	1002 ± 40.1	2.4 ± 0.12
Ar	220	30	200	--	51	76 ± 3.0	
		30	200	75	51	250 ± 10.0	
		30	200	250	51	590 ± 23.6	
		30	200	500	51	1075 ± 43.0	3.10 ± 0.18
		50	200	--	51	42.7 ± 1.71	
		50	200	75	11	338 ± 13.5	
		50	200	75	88	312 ± 12.5	
		50	200	75	51	328 ± 13.1	
		50	200	250	51	870 ± 34.8	
		50	200	500	51	1760 ± 70.4	3.14 ± 0.24
		200	200	--	51	37.3 ± 1.5	
		200	200	20	51	415 ± 16.6	
		200	200	60	51	935 ± 37.4	
		200	200	120	51	1700 ± 68.0	3.37 ± 0.33
N ₂	220	10	100	--	88	106 ± 4.2	
		10	100	50	88	200 ± 8.0	
		10	100	200	88	475 ± 19.0	
		10	100	400	88	835 ± 33.4	8.3 ± 0.55
		25	200	--	88	72 ± 2.9	
		25	200	30	88	225 ± 9.0	
		25	200	100	88	525 ± 21.0	
		25	200	200	88	1000 ± 40.0	8.25 ± 0.74
		50	300	--	88	66 ± 2.6	
		50	300	20	88	267 ± 10.7	
		50	300	60	88	625 ± 25.0	8.67 ± 0.72

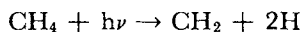
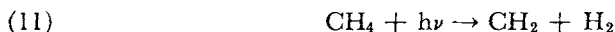
^a All reported third-order rate constants have been corrected for the contribution made by the reaction $\text{H} + \text{O}_2 + \text{CH}_4 \rightarrow \text{HO}_2 + \text{CH}_4$.

Due to the importance of the stratospheric reaction $\text{H} + \text{O}_2 + \text{N}_2 \rightarrow \text{HO}_2 + \text{N}_2$, the third-order reaction with $\text{M} = \text{N}_2$ was also investigated at 220°K, and at total pressures of 10, 25, and 50 torr. The rate constant at this temperature was determined as $(8.60 \pm 1.6) \times 10^{-32} \text{ cm}^6/\text{mole}^2\text{-s}$, and the relative efficiency for $\text{M} = \text{Ar}$ and $\text{M} = \text{N}_2$ was found to be 1:2.7.

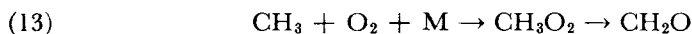
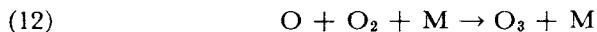
Possible systematic errors that must be considered in this study are those resulting from several possible secondary reactions involving H atoms, for example,



All of the above reactions would have caused the measured rate constant to be too high. In the case of reactions (4) and (5) both methyl and methylene radicals could be formed in primary photochemical processes (10) and (11),



Thus if reactions (4) and (5) were of major importance, it is expected that the measured third-order rate constant would have exhibited a dependence on the photoflash intensity (for both reactions $-(d\text{H}/dt) \propto I^2$). In processes (6)–(9) the second reactant is observed to be a reaction product from process (2) or from processes (12) and (13),



(Although it is known that the CH_3O_2 species eventually forms CH_2O , the exact mechanism by which this occurs is still somewhat ambiguous.) As was the case for reactions (4) and (5), therefore, the rate of loss of H atoms from reactions (6)–(9) would be directly proportional to the square power of the photoflash intensity. Thus as a test for the possible importance of any or all of the set of

reactions (4)–(9), extensive variations were made in the intensity of photoflash. These variations covered a range of a factor of eight and were carried out at three different temperatures, 220, 298, and 360°K. As can be seen from Tables II and III, within the experimental uncertainty of the measurements, no systematic deviation was observed to occur in the measured third-order rate constant.

As indicated in the above text, the set of reactions (4)–(9), if important, would have caused an increase in the observed rate constant. This was shown not to be the case. Another possibility, however, is that secondary reaction of the type



acted as a secondary source of H atoms. If so, this would have resulted in a measured rate constant which was smaller than the true rate constant. (The O atoms in reaction (14) would have been formed from the vacuum ultraviolet flash photolysis of O₂; the OH from reactions (6), (8), and/or (9).) This possibility can be discounted for the same reason as given above for reactions (4)–(9). Reaction (14) would be dependent on the square power of the flash intensity.

In addition to the preceding considerations, it should be pointed out that the accumulation of various reaction products (e.g., O₃ and CH₂O) due to multiple flashing of a single gas mixture, also can be ruled out as a source of error in this work. The evidence here again is derived from the flash intensity variation experiments in which the number of flashes per filling remained fixed in both the 88J/flash and 11J/flash experiments. In the 88J/flash experiments both ozone and formaldehyde should have reached concentrations nearly eight times greater than in the 11J/flash experiments, and hence should have had a greater influence on the measured *k* values. The observed invariance of the third-order rate constant toward an eightfold change in the flash intensity, thus, would appear to rule out any significant errors in the third-order rate constant resulting from secondary reactions.

A discussion of other systematic errors related to the use of the flash photolysis-resonance fluorescence technique has been given previously and will not be further discussed here. It has been estimated that the sum total of these errors is less than 5%.

There have been several previous measurements of the third-order rate constant *k* (H + O₂ + M) at ≈300°K (see Table IV). In two of the earliest experiments on this system, Clyne and Thrush [3] and Larkin and Thrush [7] used discharge flow systems in which H atoms were produced by an electrodeless discharge in low pressures of pure H₂ or H₂ carrier gas mixtures. In the work of Larkin and Thrush [7] the concentration of H atoms was then determined along the length of the flow reactor using a movable calorimetric probe. Clyne and Thrush [3], on the other hand, followed the change in the H atom concentration by means of adding small amounts of nitric oxide upstream from a fixed observation point and observing the resulting infrared emission from HNO. With argon acting as the third body gas, Clyne and Thrush [3] obtained a *k* value only 12%

TABLE IV. Summary of rate data on the reaction $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$.

T (°K)	M	k_M cm ⁶ molec ⁻² s ⁻¹	Technique	Reference
298	He	$(1.88) \times 10^{-32}$	Flash-photolysis resonance Fluorescence	This study (1972)
298	H ₂	$(5.90) \times 10^{-32}$		
298	CH ₄	$(42.0) \times 10^{-32}$		
298	Ar	$(1.95) \times 10^{-32}$		
220	Ar	$(3.20) \times 10^{-32}$		
220-360	Ar	$(6.75) \times 10^{-33} \exp(685 \text{ cal mol}^{-1}/RT)$		
298	N ₂	$(5.46) \times 10^{-32}$	Discharge-Flow System, HNO Emission Detection	Clyne and Thrush [5] (1963)
220	N ₂	$(8.60) \times 10^{-32}$		
293	Ar	2.2×10^{-32}		
244	Ar	$(4.0) \times 10^{-32}$		
255	Ar	$(3.5) \times 10^{-32}$		
293	He	2.1×10^{-32}		
293	H ₂ O	$52 (\pm 40\%) \times 10^{-32}$		
250-800	Ar	$1.3 \times 10^{-33} \exp(1600 \text{ cal mol}^{-1}/RT)$		
293	Ar	3.7×10^{-32}		
293	He	6.0×10^{-32}	Discharge-Flow Calorimetric Probe	Larkin and Thrush [9] (1964)
293			Mass Spec Probe of Diffusion Cloud	Dodonov Lavrovskaya and Talroze [15] (1969)
298	H ₂	4.7×10^{-32}	Pulse Radiolysis Fast Lyman- α Absorption Spectrophotometry	Bishop and Dorfman [13] (1970)
298	Ar	1.64×10^{-32}		
298	H ₂	4.7×10^{-32}	Pulse Radiolysis Fast Lyman α Absorption Spectrophotometry	Hikida, Eyre and Dorfman [14] (1971)
298	Ar	1.64×10^{-32}		
298	CH ₄	24.6×10^{-32}	Flash Photolysis resonance Fluorescence	Kurylo [16] (1972)
298	Ar	1.57×10^{-32}		
213	He	1.93×10^{-32}		
293	He	1.57×10^{-32}		
357	He	1.25×10^{-32}		
203-404	He	$6.66 \times 10^{-33} \exp[473 \text{ cal mol}^{-1}/RT]$		
298	N ₂	5.33×10^{-32}		
226	N ₂	8.7×10^{-32}		
297	Ar	1.54×10^{-32}	Discharge-Flow ESR	Mortgat and Allen
297	He	1.49×10^{-32}		
297	H ₂	6.32×10^{-32}		
298	Ar	1.87×10^{-32}	Discharge-Flow ESR	Westenberg and deHaas
298	He	1.87×10^{-32}		
300	He	0.75×10^{-32}	H ₂ -Hg photosensitization Lyman- α photometry	Ahumada, Michael and Osborne [15] (1972)
300	Ar	0.60×10^{-32}		
300	H ₂	1.20×10^{-32}		
300-2000	Ar	$4.42 \times 10^{-33} \exp[1000 \text{ cal mol}^{-1}/RT]$		Recommended value from the Review by Baulch, Drysdale, and Lloyd (1969)
298	Ar	$2.33 \times 10^{-32}^a$		
220	Ar	$4.28 \times 10^{-32}^a$		

Only those kinetic studies of the $\text{H} + \text{O}_2 + \text{M}$ system in the vicinity of room temperature or below have been listed here, the high-temperature work by several investigators being reviewed by Baulch et al. [1].

^a Calculated from the corresponding Arrhenius expression.

higher than that reported in this study, well within the combined experimental uncertainties. In the investigation by Larkin and Thrush [7] the third body Ar gave a rate constant $\approx 90\%$ higher than that observed in our work at 300°K . This disagreement lies well outside of the quoted uncertainties for the two respective studies, but might be explicable in terms of uncorrected for secondary reactions in the latter study. These secondary reactions could have results from the very low ratios of $\text{O}_2:\text{H}$ that were employed in the discharge-flow study by Larkin and Thrush [7] compared to this work.

More recently reported rate constants from discharge-flow studies by Moortgat and Allen [8] and Westenberg and de Haas [9] are in good agreement with our values (within 25% or better) for all of the third bodies Ar, He, and H_2 at 300°K . In both of these investigations, the concentration of H atoms was followed by ESR spectrometry.

In another earlier study by Dodonov et al. [10] a mass spectrometer was used to probe a diffusion cloud containing H and O_2 . The rate constant measured in this study for the third body gas He was a factor of three higher than that reported here at 300°K . Considering the uncertainties in the chemistry of the above system, however, this magnitude of disagreement is not unexpected.

In all of the investigations cited so far, flow type reactor systems were utilized in setting up a time-dependent decay of H atoms in O_2 . However, in the studies by Bishop and Dorfman [11] and Hikida, Eyre, and Dorfman [12], a static reaction cell was employed and the H atoms were produced via the electron bombardment (pulse radiolysis) of H_2 . The kinetic decay of the H atoms due to reaction with O_2 was then followed by monitoring photoelectrically the absorption of Lyman- α radiation at 1216 \AA . Although two values were measured in these studies, 2.06 and $1.6 \times 10^{-32} \text{ cm}^6/\text{mole}^2\text{-s}$, the preferred value for the third body Ar was 1.6×10^{-32} . Using H_2 as the third body gas, [11] and [12] reported a rate constant of $4.7 \times 10^{-32} \text{ cm}^6/\text{mole}^2\text{-s}$. For both H_2 and Ar, therefore, the values reported by [11] and [12] are approximately 20% lower than those given in this study. Although this is within an assigned $\pm 12\%$ uncertainty for both studies, it would appear that small systematic errors have probably gone uncorrected in one or all of the three studies being compared.

Ahumada, Michael, and Osborne [13] also have reported a study in which a static reactor was employed. In their investigation H atoms were generated by the mercury photosensitization of molecular hydrogen and were detected by means of Lyman- α absorption spectrophotometry. Their km values for the third body gases H_2 , Ar, and H are factors of two to four times lower than those reported here. Although no clearcut explanation for this large discrepancy is now available, the complexities of the Hg- H_2 system might be of some significance.

The only previously reported study on the temperature dependence of reaction (2) below 300°K was that by Clyne and Thrush [3]. As indicated earlier in the text, their technique consisted of a discharge-flow system with detection of the H atoms being the infrared emission from the $\text{H} + \text{NO} \rightarrow \text{HNO} + h\nu$ reaction.

When the above authors combined their low-temperature data with other data collected at temperatures up to 800°K, an activation energy of ≈ 1600 cal/mole was derived. The uncertainty in the data over this temperature range was very large, however, and the resulting uncertainty in the activation energy was on the order of ± 700 cal/mole. A comparison, in fact, of their activation energy with that reported in this work (685 ± 128 cal/mole) shows that the two values very nearly overlap within the assigned experimental uncertainties. Although exact reasons cannot be given at this time for the general trend toward a higher activation energy in the work by Clyne and Thrush [3], the smaller working ratio of $\text{H}:\text{O}_2$ and the presence of NO undoubtedly contributed to more complex chemistry in the earlier work.

During the course of this flash photolysis-resonance fluorescence study a second investigation by Kurylo [14] was also underway at the National Bureau of Standards using the same technique. The results of Kurylo's study also are summarized in Table IV. A comparison of the two sets of data shows systematically lower values for Ar and He at both 300°K and lower temperatures of $\approx 220^\circ\text{K}$. The difference gets worse at the lower temperature, and hence gives rise to a slightly lower activation energy (473 ± 92) than reported here. Although the differences at all temperatures are within the error limits of both investigations for the gases Ar, He, H_2 , and N_2 , the fact that the same technique was employed in both studies would indicate the presence of small, uncorrected systematic errors in one or both studies. Interesting enough, the agreement between Kurylo's value for N_2 and our value is excellent ($\pm 5\%$) at both high and low temperatures, but this could be quite fortuitous due to the larger random error in both studies for this gas. The most serious discrepancy between Kurylo's work and this study occurs for the third body gas CH_4 . At 300°K the disagreement is on the order of 60%, but since both studies reported uncertainties in this rate constant of 30–40%,¹ the indicated disagreement is within the quoted experimental uncertainties.

In the review by Baulch, Drysdale, and Lloyd [1] the experimental results from some twenty-seven studies, covering a temperature range of 225–2000°K, were critically evaluated. The recommended rate expression for the more limited temperature range of 300–2000°K was given as

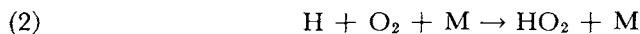
$$k_{(\text{Ar-He})} = 4.4 \times 10^{-33} \exp [1000 \text{ cal/mole}]/RT \text{ cm}^6/\text{mole-s}$$

Because of the large amount of scatter in the reviewed data, however, an uncertainty of a factor of two was assigned to the above rate expression by Baulch et al. [1]. For comparison purposes, if an extrapolation is carried out to 1000°K (several experimental measurements having been made at or near this temperature) using the rate expression from this work, a third-order rate constant for Ar of $9.5 \times 10^{-33} \text{ cm}^6/\text{mole-s}$ is calculated. The value calculated from the

¹ The much larger uncertainty in the k value for $\text{M} = \text{CH}_4$ is due to the necessity of calculating k_{CH_4} by taking the difference between two large numbers, i.e., $k_{\text{CH}_4} = k_{\text{total}} - k_{\text{Ar}}$.

rate expression of Baulch, Drysdale, and Lloyd [1] is 7.2×10^{-33} cm⁶/mole-s, within $\approx 30\%$ of this work. At 300°K, again for the third body gas Ar, the k values from this work and that calculated from [1] are 2.0×10^{-32} and 2.3×10^{-32} cm⁶/mole-s, respectively. At stratospheric temperatures (220°K), our value for Ar is seen to be approximately a factor of 1.35 lower than that extrapolated from [1]. It would appear, therefore, that the high-temperature data as reviewed by Baulch, Drysdale, and Lloyd [1] are in reasonably good agreement with the low-temperature data reported in this study.

Concerning the possible importance of these measurements to the chemical dynamics of the stratosphere, it is significant to note that to date most of the published stratospheric modeling studies have used k values for the $\text{H} + \text{O}_2 + \text{N}_2 \rightarrow \text{HO}_2 + \text{N}_2$ reaction of $3\text{--}4 \times 10^{-32}$ cm⁶/mole-s. Our value of 8.6×10^{-32} cm⁶/mole-s at 220°K would indicate that the reaction of atomic hydrogen with molecular oxygen is 2–3 times faster than previously thought. If this is correct, then in the case of the competitive set of stratospheric reactions (2) and (15),



reaction (2) would now seem to be of greater importance at midstratospheric altitudes than has heretofore been calculated.

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