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ACTIVATION ENERGIES FOR REACTIONS OF HYDROXYL RADICALS WITH HYDROGEN AND CARBON MONOXIDE

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16. Abstract

A mass-spectrometric stirred-reactor technique was used to measure the rate of the $H_2 + OH \xrightarrow{k_2} H_2O + H$ reaction at temperatures of 304, 403, and 503 K. The results yielded the rate constant $k_2 = (4.7 \pm 1.2) \times 10^{12} \exp\left[-(4200 \pm 300)/RT\right]$ $cm^3\ mole^{-1}\ sec^{-1}$. The activation energy of 4.2±0.3 kcal/mole (17.6±1.3 kJ/mole) was less than the previous estimated value of 5.15±0.15 kcal/mole (21.56±0.63 kJ/mole). The authors' previous data for the $CO + OH \xrightarrow{k_1} CO_2 + H$ reaction were reanalyzed by using the lower activation energy value for the $H_2 + OH$ reaction to obtain an improved rate expression for the $CO + OH$ reaction: $k_1 = (3.5 \pm 1.1) \times 10^{11} \exp\left[-(1120 \pm 80)/RT\right]$ $cm^3\ mole^{-1}\ sec^{-1}$.

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SUMMARY

Direct measurements of the effect of temperature on the rates of reactions of hydroxyl radicals are lacking in the literature. In the present work, rate constants for the $H_2 + OH \xrightarrow{k_2} H_2O + H$ reaction were determined at temperatures of 304, 403, and 503 K. A stirred reactor was used, and the reaction mixture was analyzed by means of a time-of-flight mass spectrometer. The results are described by the following Arrhenius expression:

$$k_2 = (4.7\pm1.2)\times10^{12} \exp\left[\frac{-(4200\pm300)}{RT}\right] cm^3 \ mole^{-1} \ sec^{-1}$$

The activation energy of 4.2±0.3 kilocalories per mole (17.6±1.3 kJ/mole) was less than previous estimates, based on indirect evidence, of about 5.15±0.15 kilocalories per mole (21.56±0.63 kJ/mole).

Earlier data obtained by the authors on the $CO + OH \xrightarrow{k_1} CO_2 + H$ reaction were reanalyzed, using the new result to correct for the effects of the simultaneously occurring $H_2 + OH$ reaction. The following, improved rate expression for the $CO + OH$ reaction was obtained:

$$k_1 = (3.5\pm1.1)\times10^{11} \exp\left[\frac{-(1120\pm80)}{RT}\right] cm^3 \ mole^{-1} \ sec^{-1}$$

INTRODUCTION

The study of elementary reactions involving the hydroxyl radical (OH) is important for a better understanding of overall combustion processes. During the last few years, various investigators (refs. 1 to 5) have made quantitative OH reaction-rate measurements. With the exception of the work of reference 4 and a previous report by the authors (ref. 5), there have been no direct measurements of the effect of temperature on OH reactions. In reference 5, a mass-spectrometric stirred-reactor method was used to measure the rate of the following reaction at temperatures of 310, 440, and 610 K:

$$CO + OH \xrightarrow{k_1} CO_2 + H \qquad \text{(I)}$$

Since the OH was generated by the reaction of partly dissociated H_2 with nitrogen dioxide (NO_2), there was competition for OH because of the reaction

$$H_2 + OH \xrightarrow{k_2} H_2O + H \qquad \text{(II)}$$

This effect was accounted for by assuming a k_2 value of $2.3\times10^{13} \exp(-5200/RT)$ cubic centimeters per mole per second recommended in reference 2. However, the rate constants deduced for reaction (I) from our high-temperature data were not the same when two different methods of data reduction were used. This suggested that the activation energy recommended for reaction (II) might be in error and also made uncertain the activation energy reported in reference 5 for reaction (I).

The present work was therefore undertaken to measure directly the activation energy for reaction (II) and to apply the result to a reanalysis of the data for the CO + OH reaction.

EXPERIMENT AND PROCEDURE

Apparatus

The 300-cubic-centimeter stirred reactor and its connection to the time-of-flight mass spectrometer are shown in figure 1. A more detailed description may be found in reference 6. As in previous work, the inside surfaces of the reactor were coated with phosphoric acid.

Gases

Hydrogen, argon, and oxygen had stated purities of at least 99.9 percent and were used without further purification. Nitrogen dioxide was about 90 percent pure and was further purified by fractionation at dry-ice temperature.

Calibration

The rate of reaction (II) was determined from measurements of H_2 and H_2O concentrations in the stirred reactor. Hydrogen (H_2) was metered, and it was only necessary to determine the sensitivity of the mass spectrometer to H_2O. To guard against possible instrument drift, at least two calibrations were made before and after a run at a given temperature.

Figure 2 is a typical calibration showing the checkpoints made before and after a kinetic run. This water calibration was performed by saturating argon with distilled water at two temperatures: near 5^o and near 15^o C. The signal at zero water concentration is due to unavoidable background and was subtracted out of the results. In general, the mass-spectrometer water calibration curves obtained before and after a run at a given temperature agreed to within ±5 percent.

The mass spectrometer was calibrated for O_2 by measuring the signals produced with metered well-mixed flows of this gas with argon.

Production of Hydroxyl Radicals

As in reference 5, OH was produced by titrating hydrogen atoms with nitrogen dioxide (ref. 1) in the stirred reactor:

$$H + NO_2 \longrightarrow OH + NO \tag{III}$$

Atomic hydrogen was made by subjecting a dilute (~2 percent) mixture of H_2 in argon to a microwave discharge. The amount of H_2 dissociated was observed to be 35 to 40 percent by monitoring the H_2 peak when the discharge was turned "off" and "on." This information was necessary for the following reasons:

(1) In the present experiment it was assumed that the initial OH concentration $\left[OH\right]_o$ is equal to the concentration of added NO_2 $\left[NO_2\right]_o$. This assumption is necessary for calculating the steady-state concentration of OH $\left[OH\right]_t$ (to be discussed in the next section). To ensure that $\left[OH\right]_o$ is equal to $\left[NO_2\right]_o$, the H atoms must always be in excess; if NO_2 is in excess, there may be further hydroxyl formation resulting from titration of H atoms formed in subsequent processes, such as $O + OH \longrightarrow O_2 + H$. To be sure of an excess of H atoms, NO_2 was added in an amount equivalent to about one-half of the H atoms produced in the discharge.

(2) The information on the dissociation of H_2 was also needed to calculate the concentration of H_2 in the reactor when more H_2 was added to study the $H_2 + OH \longrightarrow H_2O + H$ reaction.

The initial OH concentration was reduced during the time of residence in the reactor by the following two reactions, which, like reaction (III), are also very fast (ref. 7):

$$OH + OH \longrightarrow H_2O + O \qquad \text{(IV)}$$

$$O + OH \longrightarrow O_2 + H \qquad \text{(V)}$$

At room temperature and in the absence of any further additions of H_2, reaction (II) is too slow to compete with reactions (IV) and (V) for OH. Under these conditions, the residence time in the reactor was sufficient for reactions (III) to (V) to proceed close to completion with the following overall stoichiometry (ref. 7): -

$$2H + 3NO_2 \longrightarrow 3NO + H_2O + O_2 \qquad \text{(VI)}$$

Some preliminary work on the $H + NO_2$ titration confirmed equation (VI); the result is shown in figure 3. It can be seen that the amounts of H_2O and O_2 measured by the mass spectrometer are accurately equal to one-third of the added NO_2. (In fig. 3 as elsewhere in this report, flow rates reduced to standard conditions (F, cm^3/sec, at 300 K and 750 torr) are used interchangeably with concentrations, since one can be changed to the other by means of the known total flow rate.)

Inasmuch as OH could not be measured directly because its concentration in the reactor is too low, the result shown in figure 3 is important for two reasons: (1) it shows that the assumed equality of initial $[OH]_o$ to $[NO_2]_o$ is valid; and (2) it suggests that OH does not disappear, to any important extent, by ternary or wall reactions because such reactions would be unlikely to preserve the 1:3 ratios of both $H_2O:NO_2$ and $O_2:NO_2$ called for by the gas-phase reaction (VI).

Calculation of Rate Constants

$\underline{H_2 + OH \text{ reaction.}}$ - The rate of production of water in a stirred reactor in which reactions (II) and (IV) are occurring is

$$\frac{[H_2O]}{\Delta t} = k_2[H_2]_t[OH]_t + k_4[OH]_t^2 \qquad (1)$$

where Δt is the residence time in the reactor and the subscript t indicates the steady-state concentrations in the reactor. Equation (1) can be rearranged to obtain

$$k_2 = \left(\frac{[H_2O]}{\Delta t} - k_4[OH]_t^2\right)\left(\frac{1}{[OH]_t[H_2]_t}\right) \tag{2}$$

In equation (2), the quantities $[H_2O]$, $[H_2]_t$, and Δt are measured. However, as was stated earlier, $[OH]_t$ could not be measured and it was therefore necessary to calculate it in a manner similar to that used in reference 5. If it is assumed that atomic oxygen is in a steady state because of the great speed (ref. 7) of reaction (V), the rate of reaction of OH in a stirred reactor is given by

$$-\frac{\Delta[OH]}{\Delta t} = -\frac{\left([OH]_t - [OH]_o\right)}{\Delta t} = 3k_4[OH]_t^2 + k_2[OH]_t[H_2]_t \tag{3}$$

By invoking equation (1), equation (3) can be rewritten as

$$\frac{-\left([OH]_t - [OH]_o\right)}{\Delta t} = 2k_4[OH]_t^2 + \frac{[H_2O]}{\Delta t} \tag{4}$$

and

$$[OH]_t = \frac{-1 + \sqrt{1 + 8k_4\,\Delta t\left([OH]_o - [H_2O]\right)}}{4k_4\,\Delta t} \tag{5}$$

where $[OH]_o = [NO_2]_o$. This result was substituted into equation (2), which was then solved for k_2.

CO + OH reaction. - As was pointed out in reference 5, the rate constant for this reaction may be derived from the data of reference 5 in two ways. The first and more direct method follows directly from the reaction-rate expression for a stirred reactor:

$$\frac{[CO_2]}{\Delta t} = k_1[CO]_t[OH]_t \tag{6}$$

The quantity $[OH]_t$ is calculated from an expression similar to equation (5) but with an additional term accounting for the loss of OH in reaction (I):

$$\left[OH\right]_t = \frac{-\left(k_2\left[H_2\right]_t \Delta t + 1\right) + \sqrt{\left(k_2\left[H_2\right]_t \Delta t + 1\right)^2 + 12k_4 \Delta t\left(\left[OH\right]_o - \left[CO_2\right]\right)}}{6k_4 \Delta t} \qquad (7)$$

The second method makes use of the fact that each addition of CO was accompanied by a simultaneous decrease in the observed H_2O peak intensity, because of the competition for OH of reaction (I) with reactions (II), (IV), and (V). Although $\left[H_2O\right]_t$ was not measured in the work of reference 5, the change in H_2O peak $-\Delta\left[H_2O\right]$ relative to that obtained without added CO $\left[H_2O\right]_o$ was obtained. Inasmuch as

$$\left[H_2O\right]_o = k_4\left[OH\right]_t^2 \Delta t + k_2\left[OH\right]_t\left[H_2\right]_t \Delta t \qquad (8)$$

where $\left[OH\right]_t$ can be calculated by means of equation (5), $\left[H_2O\right]_t$ in the presence of added CO is given by

$$\left[H_2O\right]_t = \left[H_2O\right]_o\left(1 - \frac{\Delta\left[H_2O\right]}{\left[H_2O\right]_o}\right) \qquad (9)$$

This value for $\left[H_2O\right]_t$ can then be used together with measured quantities to derive a second value k_1' for the rate constant of reaction (I). This derivation makes use of the following relation among the rates of reactions (I), (II), and (IV):

$$\frac{k_1\left[CO\right]_t}{k_2\left[H_2\right]_t + k_4\left[OH\right]_t} = \frac{\left[CO_2\right]}{\left[H_2O\right]_t} \qquad (10)$$

And from equation (6), an expression for $\left[OH\right]_t$ is obtained:

$$\left[OH\right]_t = \frac{\left[CO_2\right]}{k_1\left[CO\right]_t \Delta t} \qquad (11)$$

From equations (10) and (11), the alternate value of the rate constant k_1' can be obtained:

$$k_1' = \frac{k_2[H_2]_t[CO_2]}{2[CO]_t[H_2O]_t}\left\{1 + \sqrt{1 + \frac{4k_4[H_2O]_t}{\left(k_2[H_2]_t\right)^2 \Delta t}}\right\} \tag{12}$$

Equation (12) is an improvement over the equation used in reference 5 to calculate k_1', because all terms in equation (12) are known, or can be easily evaluated, whereas the previous equation contained a factor that was difficult to evaluate.

RESULTS AND DISCUSSION

Rate Constants for H_2 + OH Reaction

Reaction-rate measurements of k_2 were made at or near each of the following temperatures: 304, 403, and 503 K. The experimental data and the rate constants derived from them are listed in table I. The value of k_4 needed for equations (3) and (5) was obtained by setting it equal to 1.55×10^{12} cubic centimeters per mole per second at 300 K (ref. 2), with an assumed activation energy of 1 kilocalorie per mole (4.2 kJ/mole) (ref. 1).

The rate constants listed in table I show a good deal of scatter. The reason for this is the great sensitivity of the results to the measured water concentration $[H_2O]$. Calculations made using equations (2) and (5) and assuming 10 and 20 percent errors in $[H_2O]$ showed that the errors were magnified in the resulting k_2. In general, 10 percent errors in $[H_2O]$ would produce 25 to 40 percent changes in k_2; and 20 percent errors, 40 to 60 percent changes. Furthermore, since the mass-spectrometer stability was about ±1/2 peak unit and H_2O signals were usually only about 5 to 6 peak units, there was an inherent ±10 percent uncertainty in $[H_2O]$. In table I the standard deviations show that the errors in H_2O measurements must have averaged 10 to 15 percent, at most. The results are plotted in the Arrhenius fashion in figure 4, and the least-squares line through the data yields the following expression for the rate constant:

$$k_2 = (4.7\pm1.2)\times10^{12} \exp\left[\frac{-(4200\pm300)}{RT}\right] \text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1} \tag{13}$$

The error limits quoted are based on the standard deviations for the slope and intercept of our least-squares line. The activation energy of 4.2±0.3 kilocalories per mole

(17.6±1.3 kJ/mole) changes only slightly if other values are assumed for the activation energy of reaction (IV), as shown in the following table:

Assumed activation energy, reaction (IV)		Resulting activation energy, reaction (II)	
kcal/mole	kJ/mole	kcal/mole	kJ/mole
0	0	3.5	14.7
.5	2.1	3.7	15.5
1.0	4.2	4.0	16.7
1.5	6.3	4.1	17.2
2.0	8.4	4.3	18.0

The effect of k_4 values on k_2 is also small. Analysis shows that a given percentage change in k_4 values will produce only about one-half of that percentage change in k_2.

The dashed line in figure 4 represents the recommendation of the Leeds group (ref. 8). It is based on the room-temperature results of references 1, 2, and 9, plus eight other determinations made at higher temperatures in flame, shock-tube, and ignition-limit studies. All these high-temperature data lie above the extrapolation of the line derived from the present results, and the slope of the dashed line corresponds to an activation energy of 5.15±0.15 kilocalories per mole (21.56±0.63 kJ/mole) (ref. 8).

Although the weight of the evidence seems to favor the higher activation energy, there are two facts that support the lower value. First, the only other direct determination of k_2, made in the temperature range from 813 to 843 K (ref. 10) and shown as triangles in figure 4, lie below the solid line. Second, in two shock-tube studies involving the combustion of hydrogen, observations were made that could not be explained by the "accepted" high-temperature values of k_2 but instead called for lower values (refs. 11 and 12). In reference 12, the authors commented that their experimental data supported a k_2 value of about 2.8×10^{12} exp (-3895/RT) which the authors of reference 12 obtained from N. R. Greiner in a private communication.

All but one of the eight high-temperature determinations used in reference 8 to generate the dashed line of figure 4 are, in some sense, indirect. One was a shock-tube study in which rate constants for a large number of reactions were varied to obtain a fit to observed ignition delays, and the results were not very sensitive to the rate of reaction (II). In three other studies, the ratio of k_2 to another rate constant was obtained, so that the value of the second rate constant had to be supplied in order to derive k_2. Three more used flames in which the disappearance of OH was followed, and it was assumed that all H_2 consumed was by reaction (II). The final determination also employed a flame but was more direct: free-radical concentrations were measured by electron spin resonance (ESR) spectrometry and water was determined by freezeout. However, the production of water by reaction (IV) was neglected, and the values derived for k_2 may therefore be too large.

In appears that the discrepancy between the fitted activation energy (ref. 8) and the value measured directly in this work must be resolved by redetermination of k_2 at temperatures above 1000 K.

Recalculation of Rate Constants for CO + OH Reaction

Both methods of deducing the rate constant for reaction (I) from the experimental data require that a value for k_2 be supplied in order to calculate $[OH]_t$ (eq. (7)) or $[H_2O]_t$ (eqs. (8) and (9)). In equation (12), however, k_2 appears in a more direct manner. Thus, there could be a discrepancy between k_1 and k_1' if the value assigned to k_2 is wrong.

As stated in the INTRODUCTION, a discrepancy did occur in the data obtained above room temperature and was reported in reference 5. Recalculation of the CO + OH rate constant using equations (6) and (12) and the newly obtained k_2 values (eq. (13)) showed no discrepancy between k_1 and k_1' values. This fact suggests immediately that equation (13) may be more correct than $k_2 = 2.3\times10^{13} \exp(-5200/RT)$ (ref. 2); but a recalculation of k_1' values using the latter k_2 and equation (12) from the present work also showed very good agreement in k_1 and k_1' values. This latter result must mean that the equation used to calculate k_1' values in reference 5 was inadequate.

It was noted in reference 5 that k_1 decreased as the CO concentration in the stirred reactor increased. Recent sampling experiments involving CO and H_2 showed that CO can produce this effect because CO reduced mass-spectrometer sensitivity to other mass peaks more than did H_2. Thus, the greater the CO concentration in the sample, the smaller the ion current for a given mass peak. To correct for this effect, the recalculated k_1 and k_1' for each temperature were plotted against $[CO]$, as in reference 5; and a least-squares line was drawn through each set of data to obtain the rate constants at zero CO concentration. The results are as follow:

Temperature, K	Rate constant, $cm^3\ mole^{-1}\ sec^{-1}$	
	k_1	k_1'
310	5.6×10^{10}	5.9×10^{10}
440	10.1	10.7
610	13.6	13.3

These data form an excellent straight line in an Arrhenius diagram and are represented by the following expression:

$$k_1 = (3.5\pm1.1)\times10^{11}\ \exp\left[\frac{-(1120\pm80)}{RT}\right]\ cm^3\ mole^{-1}\ sec^{-1} \tag{14}$$

Error limits quoted are standard deviations for the slope and intercept of the least-squares line.

The activation energy of 1.12 kilocalories per mole (4.69 kJ/mole) does not differ greatly from the previously reported (ref. 5) value of 1.2 kilocalories per mole (5.02 kJ/mole), but is considered more reliable in view of the close agreement between k_1 and k_1' that now exists. The only other reported, but still unpublished, direct measurement of the activation energy for reaction (I) yielded 0±1 kilocalorie per mole (0±4.2 kJ/mole) (ref. 13), in satisfactory agreement with the present value. A critical analysis of all data available on this reaction up to 1968 (ref. 14) led to a recommended activation energy of 1.08 kilocalories per mole (4.52 kJ/mole), which differs negligibly from 1.12. Thus, the temperature dependence of k_1 seems well established.

However, reanalysis of the data has done nothing toward increasing the 300 K value of k_1, which is only about 65 percent as big as several other direct determinations made at room temperature and summarized in reference 14. This difference is outside the experimental error. A possible explanation suggested in reference 5 is that mixing is incomplete in the stirred reactor because of the speed of the reactions occurring. But upon reflection this explanation seems less likely. For a stirred reactor to work properly, the mixing time must be considerably less than both the residence time and the characteristic reaction time of the most rapid reaction. Under the conditions of these experiments, even the random-walk diffusion time is considerably less than the reaction time and only one-tenth the residence time. In addition, the entering gas velocity is so high that an average gas particle makes more than 40 traverses before it exits from the reactor, and efficient mixing must have been attained. Thus, it is hard to attribute our differences from the results of others to poor mixing, and the reason for the discrepancy remains unclear.

Note Added in Proof

Recently, N. R. Greiner's work on the $H_2 + OH \xrightarrow{k_2} H_2O + H$ and $CO + OH \xrightarrow{k_1} CO_2 + H$ reactions using a spectroscopic technique was published (ref. 15). For the temperature range of 300 to 500 K, rate constants k_2 and k_1 were determined to be $(4.06\pm1.26)\times10^{12} \exp\left[-(4020\pm180)/RT\right]$ and $(1.26\pm1.18)\times10^{11} \exp\left[-(230\pm140)/RT\right]$ cubic centimeters per mole per second, respectively. Greiner's k_2 value is in excellent agreement with that reported in the present investigation. The disagreement in k_1 value is not surprising since the k_1 value at 300 K in the present investigation was much lower than those reported by several other workers.

SUMMARY OF RESULTS

Rate constants for the reaction $H_2 + OH \longrightarrow H_2O + H$ were measured at temperatures of 304, 403, and 503 K. The room-temperature result was close to other values in the literature but the activation energy, measured directly for the first time, was 4.2±0.3 kilocalories per mole (17.6±1.3 kJ/mole), which was less than the Leeds group's estimate of 5.15±0.15 kilocalories per mole (21.56±0.63 kJ/mole) that was based on indirect evidence. Reanalysis of previous $CO + OH \longrightarrow CO_2 + H$ data by using either the newly determined activation energy or the previous energy of 5.2 kilocalories per mole (21.8 kJ/mole) for k_2 brought the two sets of CO + OH rate constants into essentially perfect agreement and established the activation energy of this reaction as 1.12 kilocalories per mole (4.69 kJ/mole). The discrepancy in the previous high-temperature $CO + OH \longrightarrow CO_2 + H$ data was due to the fact that the previous equation that was used to calculate k_1' was inadequate.

The Arrhenius expressions obtained for the rates of these two reactions were as follows:

$$H_2 + OH: \quad k_2 = (4.7 \pm 1.2) \times 10^{12} \exp\left[\frac{-(4200 \pm 300)}{RT}\right] \mathrm{cm}^3\ \mathrm{mole}^{-1}\ \mathrm{sec}^{-1}$$

$$CO + OH: \quad k_1 = (3.5 \pm 1.1) \times 10^{11} \exp\left[\frac{-(1120 \pm 80)}{RT}\right] \mathrm{cm}^3\ \mathrm{mole}^{-1}\ \mathrm{sec}^{-1}$$

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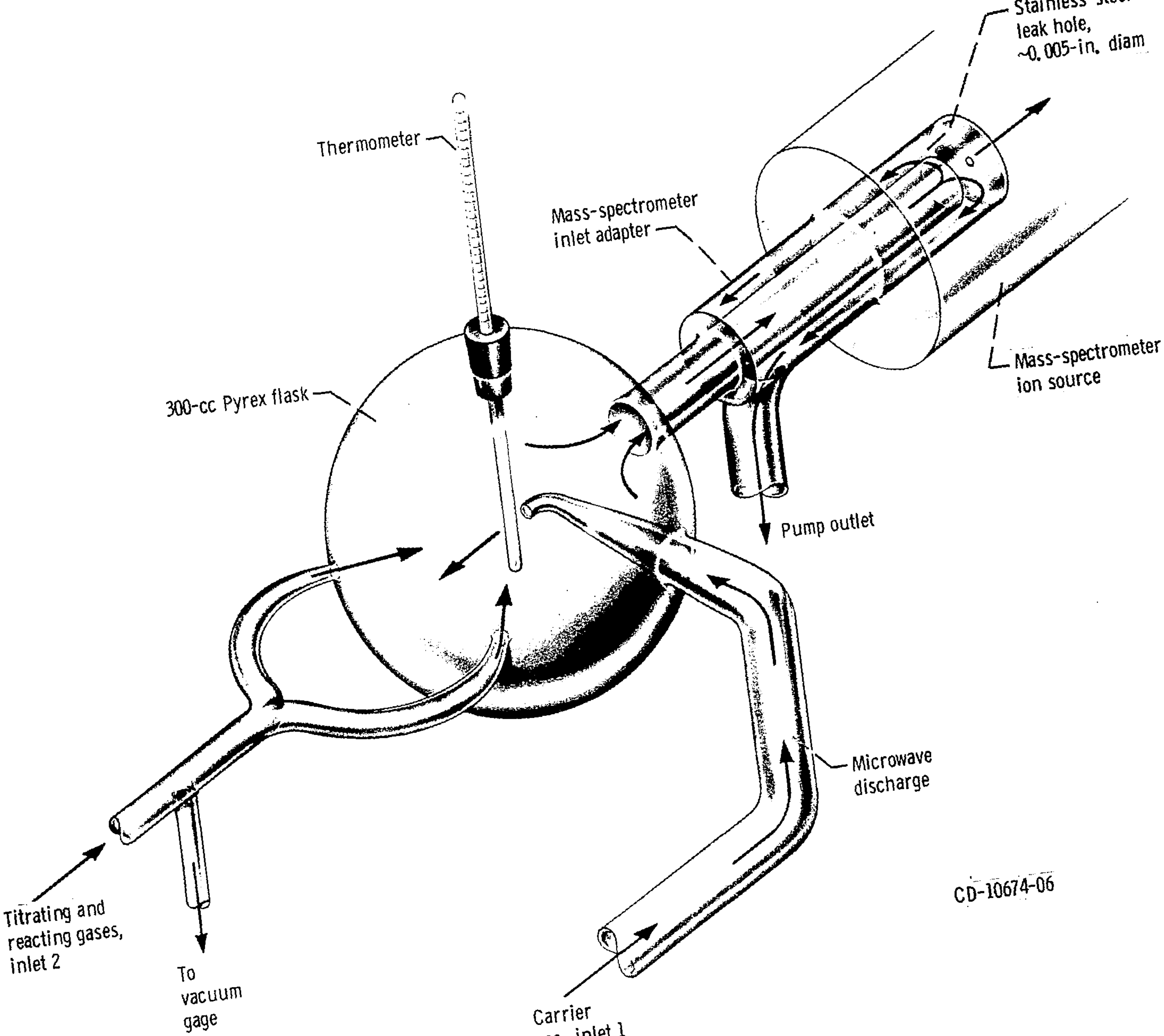
TABLE I. - RATE MEASUREMENT DATA FOR OH + H_2 REACTION

Run	Hydrogen concentration, $[H_2]_t$, moles/cm^3	Nitrogen dioxide concentration (initial OH concentration $[OH]_0$), moles/cm^3	Total water concentration, $\Delta[H_2O]$, moles/cm^3	Residence time, Δt, sec	Temperature, K	Rate constant, k_2, cm^3 mole^{-1} sec^{-1}
1a	35×10^{-10}	2.65×10^{-10}	1.06×10^{-10}	0.168	304	3.6×10^9
1b	121	2.36	1.05	.150	↓	1.7
1c	118	2.38	1.06	.151	↓	1.7
1d	94	2.23	1.07	.155	↓	2.7
1e	86	2.75	1.39	.156	↓	3.8
1f	80	2.80	1.36	.159	↓	3.5
1g	76	3.10	1.40	.158	↓	3.1
1h	71	3.15	1.90	.161	↓	8.1
1i	64	3.06	1.78	.162	↓	7.8
1j	65	3.05	1.97	.161	↓	10.4
1k	63	3.03	1.76	.160	↓	8.0
					Average	5.0×10^9 (σ = 3.0)
2a	22×10^{-10}	2.88×10^{-10}	1.86×10^{-10}	0.126	403	42×10^9
2b	21	2.84	1.74	.125	↓	37
2c	46	2.65	2.03	.117	↓	34
2d	46	2.75	1.97	.121	↓	27
2e	43	2.78	2.12	.122	↓	36
2f	41	2.46	1.79	.123	↓	30
2g	40	2.43	1.88	.122	↓	38
2h	45	2.43	1.96	.121	↓	40
					Average	36×10^9 (σ = 4)
3a	15×10^{-10}	1.50×10^{-10}	1.12×10^{-10}	0.106	501	90×10^9
3b	15	1.50	1.07	.106	501	77
3c	15	1.50	1.08	.105	501	77
3d	21	1.48	1.10	.104	503	63
3e	21	1.48	1.13	.104	503	66
3f	27	2.40	1.65	.102	504	48
3g	29	2.41	1.64	↓	↓	43
3h	25	2.41	1.79	↓	↓	65
3i	25	2.12	1.58	↓	↓	61
3j	23	2.06	1.57	.104	↓	71
3k	27	1.88	1.57	.102	↓	83
3l	27	1.89	1.45	.102	↓	61
3m	23	1.58	1.27	.104	↓	76
3n	24	1.58	1.14	.104	↓	50
3o	42	1.51	1.26	.0996	↓	49
					Average	65×10^9 (σ = 11)



nection to mass spectrometer.

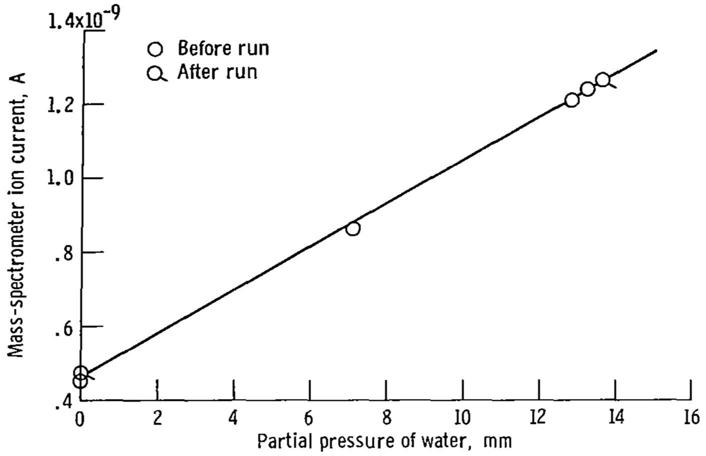


Figure 2. - Mass spectrometer sensitivity to water. Hydrogen-argon gas mixture saturated with water at 15° and 5° C.

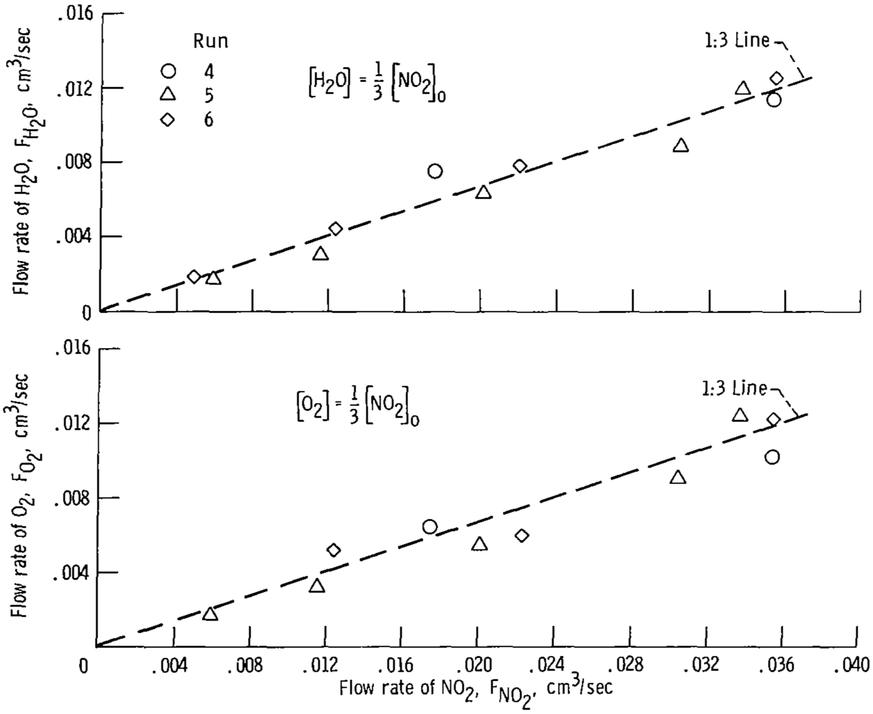


Figure 3. - Mass spectrometer monitoring water and oxygen during $H + NO_2 \longrightarrow NO + H$ titration reaction at 310 K.

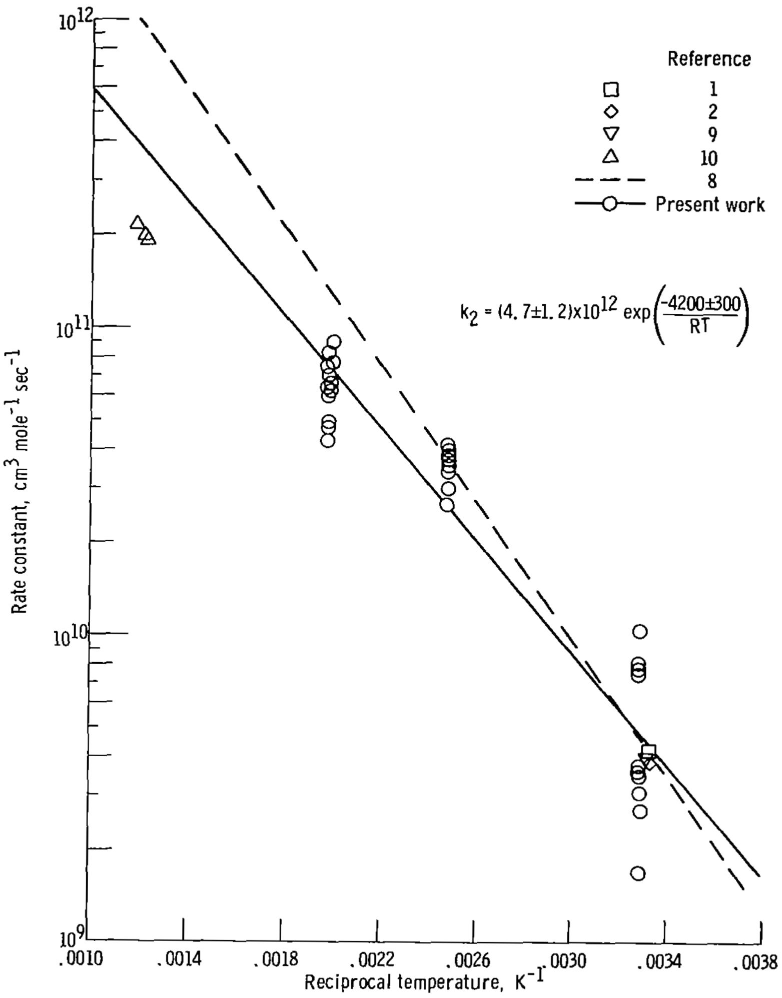


Figure 4. - Rate constants for $H_2 + OH \longrightarrow H_2O + H$ reaction.