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SUMMARY

Rate constants of four elementary bimolecular reactions have been determined by monitoring the exponential growth of CO flame band emission behind incident shocks in four suitably chosen gas mixtures. Results are as follows: $OH + H_2 \longrightarrow H_2O + H$, $k_1 = 2.1\times10^{13}\exp(-5.1 \text{ kcal/RT})$ $\text{cm}^3\text{mol}^{-1}\text{sec}^{-1}$ (1100-1600°K); $H + O_2 \rightarrow OH + O$, $k_2 = 1.25\times10^{14}\exp(-16.3 \text{ kcal/RT})$ (1150-1400°K); $O + H_2 \longrightarrow OH + H$, $k_3 = 2.96\times10^{13}\exp(-9.8 \text{ kcal/RT})$ (1200-1600°K); and $OH + CO \longrightarrow CO_2 + H$, $k_5 = 4.2\times10^{11}\exp(-1.0 \text{ kcal/RT})$ (1300-1900°K). Less directly, by analysis of early, linear luminosity and times to 50% of peak light intensity, the rate of the initiation reaction, $CO + O_2 \longrightarrow CO_2 + H$ is estimated to be $k_6 = 1.6\times10^{13}\exp(-41 \text{ kcal/RT})$.

INTRODUCTION

When a mixture containing hydrogen, carbon monoxide and oxygen is subjected to a temperature and pressure pulse in a shock tube small concentrations of atoms and free radicals are first formed by processes such as

$$CO + O_2 \longrightarrow CO_2 + O$$
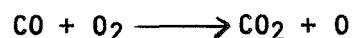
These concentrations may then grow exponentially via the well-known branched chain scheme,

$$OH + H_2 \xrightarrow{k_1} H_2O + H \qquad\qquad (I)$$

$$H + O_2 \xrightarrow{k_2} OH + O \qquad\qquad (II)$$

$$O + H_2 \xrightarrow{k_3} OH + H \qquad\qquad (III)$$

$$H + O_2 + M \xrightarrow{k_4} HO_2 + M \qquad\qquad (IV)$$

$$OH + CO \xrightarrow{k_5} CO_2 + H \qquad\qquad (V)$$

Theory shows[1,2] that the oxygen atom concentration increases as $[O] \cong A \exp \lambda t$ (except very early in the reaction), where λ is the positive root of the cubic equation

$$\lambda^3 + (\nu_1 + \nu_2 + \nu_3 + \nu_4 + \nu_5)\lambda^2 + [(\nu_1 + \nu_5)(\nu_3 + \nu_4) + \nu_3\nu_4]\lambda$$
$$- \nu_3(\nu_1 + \nu_5)(2\nu_2 - \nu_4) = 0 \qquad\qquad (1)$$

Here $\nu_1 \equiv k_1[H_2]$, $\nu_2 \equiv k_2[O_2]$, $\nu_3 \equiv k_3[H_2]$, $\nu_4 \equiv k_4[O_2][M]$, and $\nu_5 \equiv k_5[CO]$. Thus the exponential growth constant λ depends on the gas composition and the rate constants of reactions I - V. In this paper we report measurements on mixtures chosen to permit determinations of the rates of reactions I, II, III and V. Mixtures were selected by analyzing Eq.(1).

EXPERIMENTAL ASPECTS

Growth constants were obtained by measuring the blue CO flame band emission behind incident shocks. The intensity of this radiation is proportional to the product of carbon monoxide and oxygen atom concentrations[3] and since very little CO is consumed, the light monitors the increase of oxygen atom concentration with time. Details of the shock tube and associated optical and electronic equipment are described elsewhere[4].

Gas mixtures contained varying amounts of H_2, CO, O_2, and in some mixtures CO_2 diluted five- to tenfold with Ar. Hydrogen, oxygen, and argon

were high purity tank gases and were used without further purification. Carbon monoxide was condensed at liquid nitrogen temperature; about one quarter of the condensate was pumped off and discarded. Dry ice served as a convenient source of carbon dioxide. It was purified by subliming three quarters of a sample into a liquid nitrogen cooled trap. The first quarter of this trapped fraction was discarded and the middle half used for mixture preparation.

Recently[4] it has been shown that boundary layer effects must be considered in analyzing data obtained behind incident shocks; the growing boundary layer causes increases in temperature, density, and residence time with increasing distance behind the shock. Conditions behind the shocks, in the region of the experimental measurements, were obtained from a computer program which integrated the equations of chemical change for a shocked gas accounting for the effects of boundary layer buildup; the procedure has been set forth in detail in reference 4. In general, the extent of chemical reaction was small and changes in gas properties were brought about largely by the gas dynamics associated with boundary layer growth.

Exponential growth constants were obtained from plots of the logarithm of observed light intensity versus gas time; the relation between gas and laboratory times was obtained from the computer calculations.

SELECTION OF GAS MIXTURES

Let us turn now to the rationale used to select gas mixtures by analysis of Eq.(1). To begin with, under our experimental conditions $\mathcal{D}_4$ is generally small in comparision with the other $\mathcal{D}$ and can be neglected for

purposes of a qualitative discussion. Secondly, λ turns out to be a small positive root - of the order of the smaller ν values and small compared with the larger ν values. Thus we neglect λ^3 in comparison with the other terms and rewrite Eq.(1)

$$\left[(\nu_1 + \nu_5) + \nu_2 + \nu_3\right]\lambda^2 + \nu_3(\nu_1 + \nu_5)\lambda \cong 2\nu_2\nu_3(\nu_1 + \nu_5) \quad (2)$$

If the amount of hydrogen in a mixture is large in comparison to oxygen, ν_1 and ν_3 are large and the term involving λ^2 may be neglected; in this event

$$\lambda \cong 2\nu_2 \quad (3)$$

On the other hand, if only a trace of hydrogen is present, ν_3 is small, the term involving λ may be neglected, and

$$\lambda^2 \approx \frac{2\nu_2\nu_3(\nu_1 + \nu_5)}{\nu_2 + (\nu_1 + \nu_5)} \quad (4)$$

If we choose a mixture with a large amount of carbon monoxide, ν_5 is large and

$$\lambda \sim \sqrt{2\nu_2\nu_3} \quad (5)$$

Whereas if there is a large amount of oxygen, $_2$ is large and

$$\lambda \sim \sqrt{2\nu_3(\nu_1 + \nu_5)}$$
$$\longrightarrow \sqrt{2\nu_3\nu_1} \qquad\qquad [H_2] > [CO] \quad (6)$$
$$\longrightarrow \sqrt{2\nu_3\nu_5} \qquad\qquad [CO] > [H_2]$$

This, then, outlines a strategy for obtaining rates of reactions I, II, III, and V. First a mixture rich in hydrogen is used to determine k_2. Next, with k_2 known a mixture with a trace of hydrogen and rich in carbon monoxide is used to determine k_3. Finally with k_3 known, mixtures with

excess oxygen and varying proportions of hydrogen and carbon monoxide are used to isolate k_1 and k_5.

The forgoing discussion indicates a qualitative procedure for selecting gas mixtures. However, we also need a quantitative measure of the sensitivity of the growth constant for a particular mixture to the various rate constants. For example, we know that to isolate k_3 we want a mixture with a trace of hydrogen, a small amount of oxygen, and carbon monoxide in excess. But for a candidate composition, is the hydrogen concentration small enough, and is carbon monoxide sufficiently in excess? A quantitative measure of the sensitivity to the various rates can be obtained by logarithmic partial differention of Eq.(1). For example,

$$\left(\frac{\partial \ln \lambda}{\partial \ln \nu_3}\right) = \frac{1}{2}$$

$$- \frac{1}{2} \frac{\lambda^2 + 2\nu_3\lambda + (\nu_1 + \nu_5)(\nu_3 - \nu_4) + \nu_3\nu_4}{3\lambda^2 + 2(\nu_1 + \nu_2 + \nu_3 + \nu_4 + \nu_5) + (\nu_1 + \nu_5)(\nu_3 + \nu_4) + \nu_3\nu_4} \tag{7}$$

Equation (7) shows the growth constant will depend on something less than the square root of ν_3 - a somewhat weaker dependence than that suggested by Eq.(5).

The mixture compositions selected are shown in Table I along with sensitivities calculated for a pressure of one atmosphere and temperatures near the mid points of the ranges of the experimental data. These mixtures were chosen on the basis of: 1) high sensitivity to the rate constant being determined, 2) minimized sensitivity to the other rate constants, 3) growth constant in a convenient range for measurement (5×10^3 to $7 \times 10^4 \text{sec}^{-1}$), 4) and/sufficient content of minor, rate limiting constituents to permit accurate mixture preparation.

It was necessary to include in each mixture sufficient infrared-active gas so that the arrival of the contact surface could be detected by the cessation of infrared emission. (The position of the contact surface between driver and driven gas is needed in the boundary layer analysis.) Mixtures 2, 3 and 5 have substantial carbon monoxide concentrations; carbon dioxide was added to mixture 1 to achieve adequate infrared activity. Carbon dioxide was also added to mixtures 3 and 5, to ensure vibrational relaxation of the carbon monoxide. (In preliminary experiments on a composition similar to mixture 3, but without CO_2, carbon monoxide was not relaxed and rate constants gave an activation energy of 15 kcal for reaction 3, much higher than literature values[5]. Results from mixture 3, with added CO_2, show that the preliminary data were too low, particularly at the lower temperatures.)

CALCULATION OF RATE CONSTANTS
FROM EXPONENTIAL GROWTH CONSTANTS

Rate constants were obtained from the experimental growth constants by means of Eq.(1), rearranged and solved for the rate constant being sought from the mixture in question - k_2 from mixture 2, k_3 from mixture 3, etc. Mixture 2 was studied first, because the growth constants for this mixture depend almost exclusively on k_2 and are only slightly affected by the rates of the other reactions - see Table I. Values of γ_4 were calculated from the k_4 suggested by the Leeds Group[6]. Trial values of k_1, k_3, and k_5 were also taken from the Leeds recommendations[5,6,7], but final values were taken from our own determinations. This involves an iterative procedure, since our values of k_3 depend, in turn, on our values k_2, and

to a lesser extent k_5. Two iterations sufficed to establish k_2.

Next k_3 was obtained by analyzing the growth constants for mixture 3, then k_1 from mixture 1, and finally k_5 from mixture 5. Three iterations around the k_3-k_1-k_5 loop were required.

A least squares fit to the Arrhenius equation was made for each set of rate constants; these equations were then used in subsequent calculations.

RESULTS AND DISCUSSION

The experimental results will be discussed in the order in which the data were obtained - first k_2, followed by k_3, k_1 and k_5. This is also, approximately, in order of decreasing precision.

Rate constants for reaction II are presented in Table II. The temperatures and pressures, obtained from the boundary layer analysis, are average values for period during which λ was measured; during this period the temperature varied by less than 10° and the pressure by less than one percent. Rate constants are plotted versus reciprocal temperature in Fig. 1. The least squares line through the data is

$$k_2 = 1.25 \times 10^{14} \exp(-16.3 \text{ kcal/RT}) \text{cm}^3 \text{mole}^{-1} \text{sec}^{-1} \tag{8}$$

The standard deviation[8] of $\ln k_2$ is ± 0.094, or about 10%; the standard deviation[8] of the activation energy is 1.1 kcal. Rates given by Eq. (8) fall somewhat below most previous high temperature $(T > 1000^O K)$ determinations and as a consequence lie about 30% below the recommendation of the Leeds group[6], but well within their suggested error limit of ± 50 percent. The activation energy of 16.3 kcal is slightly more than the endothermicity of reaction II, 16.15 kcal at $1300^O K$, in contrast to several other recent shock tube studies[6,9] which have yielded substantially lower activation

energies. Indeed, Eq. (8) extrapolated to room temperature predicts rate constants which are straddled by the discordant results of Clyne and Thrush[10] and Kaufman and Del Greco[11].

It should be emphasized that these satisfying results are obtained only when the effects of boundary layer growth are considered. If we ignore the boundary layer by using the temperature and pressure immediately behind the shock in the data reduction, rate constants for reaction II are 20-60 percent larger with an apparent activation energy of only 11.9 kcal.

Rate constants for reaction III are shown in Table III and also plotted in Fig. 1. The least squares line through the data is

$$k_3 = 2.96 \times 10^{13} \exp(-9.8 \text{ kcal/RT}) \text{cm}^3 \text{mole}^{-1}\text{sec}^{-1}. \tag{9}$$

The standard deviation of $\ln k_3$ is $\pm$ 0.184, or about 20 percent; the standard deviation of the activation energy is 1.3 kcal. It is to be expected that errors in k_3 are roughly double those for k_2, since for mixture 3 the growth constants depend on the 0.4 power of k_3, whereas for mixture 2 the growth constants are very nearly proportional to k_2 (see sensitivities of Table I).

Rates calculated from Eq. (9) fall among other high temperature determinations[5]; they are about 50 percent above the Leeds recommendation[5] which is somewhat outside their suggested error limit of $\pm$ 30 percent. (The Leeds recommendation appears to be based almost entirely on data from temperatures below 900 K.) On the other hand Eq. (9) is only about 10 percent above an extrapolation of the more recent data of Westenberg and de Haas[12]. The activation energy of 9.8 kcal appears reasonable since it lies between the recommendations of the Leeds group (9.45 kcal) and Westenberg and de Haas (10.2 kcal). As a consequence, Eq. (9)

extrapolated to much lower temperatures predicts rate constants generally in accord with other experiments[5].

Rate constants for reaction I are shown in Table IV and also plotted versus reciprocal temperature in Fig. 2. The solid least squares line through the data is

$$k_1 = 1.9 \times 10^{13} \exp(-4.8 \text{ kcal/RT}) \text{cm}^3 \text{mole}^{-1} \text{sec}^{-1} \tag{10}$$

The standard deviation of $\ln k_1$ is ± 0.41, or about 40 percent; the standard deviation of the activation energy is 1.7 kcal.

In the temperature range of the experimental data, 1100-1600°K, Eq. (10) is in near-perfect accord with the Leeds recommendation[5]. The activation energy is somewhat lower than the 5.15 kcal suggested by Leeds, so that Eq. (10) extrapolated to room temperature predicts rate constants about 50 percent too high. We rectify this by including in the least squares analysis a recent value of $k_1 = 4.1 \times 10^9$ at 300°K due to Greiner[13]. This gives

$$k_1 = 2.1 \times 10^{13} \exp(-5.1 \text{ kcal/RT}) \text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}. \tag{11}$$

The standard deviation of $\ln k_1$ remains ± 0.41, but the standard deviation of the activation energy is reduced to 0.3 kcal. Equation (11) is shown as a dashed line in Fig. 2. Equations (10) and (11) differ by less than 4 percent in the experimental temperature range.

Rate constants for reaction V are presented in Table V and plotted in Fig. 2. The solid least squares line through the data is

$$k_5 = 1.0 \times 10^{12} \exp(-3.7 \text{ kcal/RT}) \text{cm}^3 \text{mole}^{-1} \text{sec}^{-1}. \tag{12}$$

The standard deviation of $\ln k_5$ is ± 0.28, or about 30 percent; the

standard deviation of the activation energy is 1.9 kcal. In the temperature range of 1300°-1900°K Eq. (12) gives rate constants 10-35 percent below the Leeds recommendation[7]. The 3.7 kcal activation energy is almost certainly too large; recent low temperature studies[13,14] suggest 0.2-1.0 kcal. By including in the least squares analysis Greiner's[13] recent 300°K value $k_5 = 8.6 \times 10^{10}$ we obtain

$$k_5 = 4.2 \times 10^{11} \exp(-1.0 \text{ kcal}/RT) cm^3 \text{mol}\bar{e}^1 sec^{-1}. \tag{13}$$

The standard deviation of $\ln k_5$ remains about the same, $\pm$ 0.29, but the standard deviation of the activation energy is only 0.2 kcal. Equation (13) is shown as a dashed line in Fig. 2. To the eye, Eq. (13) seems almost as good a representation of the data as Eq. (12). In the experimental temperature range Eqs. (12) and (13) differ by at most 15 percent. All-in-all, Eq. (13) seems preferable.

In addition to the rates of reactions I, II, III, and V we can make an estimate of the rate of the initiation reaction

$$CO + O_2 \xrightarrow{k_6} CO_2 + O \tag{VI}$$

The experimental light emission data for mixture 3 provide a means of obtaining the activation energy for this reaction. In these experiments light emission increased linearly with time for a short period after the shock, before an exponential increase in intensity signaled the onset of rapid chain branching. Since the early luminosity is a result of reaction VI and subsequently

$$CO + O \xrightarrow{k_7} CO_2 + h\nu, \tag{VII}$$

the increase of light emission with time is

$$\frac{dI}{dt} \propto k_6 k_7 [CO]^2 [O_2] \tag{14}$$

Consequently the slopes of luminosity-time plots were obtained and divided by the cube of the density. The logarithm of this quantity plotted against reciprocal temperature gave a straight line from the slope of which $E_6 + E_7 = 43.8$ kcal was derived, with a standard deviation of 2.1 kcal. If $E_7 = 2.6$ kcal[7], $E_6 = 41$ kcal. This is less than the 48-51 kcal activation energy inferred[2,15] from the data of Sulzmann, Myers, and Bartle[15], but larger than the 29 ± 11 kcal derivable from a recent determination[16] of the rate of the reverse of reaction VI.

It is possible to estimate actual values of k_6 using low gain light emission-time records obtained on mixture 5. These records, not suitable for determining exponential growth constants, show light emission rising to a broad maximum followed by a slow decline. Computer runs for the integrated kinetics show similar behavior for the carbon monoxide-oxygen atom concentration product. A little numerical experimentation on the computer revealed that time to maximum intensity, or better, the time to half of the peak intensity, depends on the rate of reaction VI. Consequently it was assumed the activation energy of reaction VI is 41 kcal and computer runs were made with a range of values of the preexponental factor in the Arrhenius equation so as to fit observed times to 50 percent peak light intensity. In this fashion we obtain

$$k_6 = 1.6 \times 10^{13} \exp(-41 \text{ kcal}/RT) \text{cm}^3 \text{mole}^{-1} \text{sec}^{-1} \qquad (15)$$

with a standard deviation in $\ln k_6$ of ± 0.54, which is a factor of 1.7. This is more than an order of magnitude larger than previous estimates[2,15] of this rate. On the other hand, if we used Eq. (15) to calculate the

rate of the reverse of reaction VI at $3000^\circ K$ we obtain a rate only 30 percent below the recent measurements of Clark, Garnett, and Kistiakowsky[16].

We believe Eq. (15) is an improved estimate of the rate of reaction VI. However, it has been determined in a rather indirect fashion, so that it remains suspect; definitely not as reliable as our measurements of the rates of reactions I, II, III, and V.

CONCLUDING REMARKS

In this paper we have shown how to make systematic measurements so as to isolate the rates of individual bimolecular reaction steps in the complex of six reactions which describe the ignition behavior of the hydrogen-carbon monoxide-oxygen system.

We have obtained what we believe are quite accurate measurements of the rates of the reactions $H + O_2 \longrightarrow OH + O$ and $O + H_2 \longrightarrow OH + H$. An essential has been a proper accounting of the effects of boundary layer growth on the pressure, temperature, and residence time behind the shock wave. Our measurements of the rates of $OH + H_2 \longrightarrow H_2O + H$ and $OH + CO \longrightarrow CO_2 + H$ are less precise but are perhaps the most direct determinations of these rates for temperatures above $1100^\circ K$ (previous high temperature determinations of these rates have been based on flame sampling). Finally, we have estimated the rate of the initiation reaction $CO + O_2 \longrightarrow CO_2 + O$.

REFERENCES

1. BROKAW, R. S.: Tenth Symposium (International) on Combustion, p. 269, The Combustion Institute, 1965.

2. BROKAW, R. S.: Eleventh Symposium (International) on Combustion, p. 1063 The Combustion Institute, 1967.

3. CLYNE, M. A. A. AND THRUSH, B. A.: Proc. Roy. Soc. (London), A269, 404 (1962).

4. BELLES, F. E., AND BRABBS, T. A.: Thirteenth Symposium (International) on Combustion, p.   , The Combustion Institute, 1971.

5. BAULCH, D. L., DRYSDALE, D. D., AND LLOYD, A. C.: High Temperature Reaction Rate Data, Dept. of Physical Chemistry, The University, Leeds. No. 2, Nov. 1968.

6. BAULCH, D. L., DRYSDALE, D. D., AND LLOYD, A. C.: High Temperature Reaction Rate Data, Dept. of Physical Chemistry, The University, Leeds. No. 3, April 1969.

7. BAULCH, D. L. DRYSDALE, D. D., AND LLOYD, A. C.: High Temperature Reaction Rate Data, Dept. of Physical Chemistry, The University, Leeds. No. 1, May 1968.

8. YOUDEN, W. J.: Statistical Methods for Chemists, John Wiley, New York, 1951, p. 42.

9. SCHOTT, G. L.: Twelfth Symposium (International) on Combustion, p. 569, The Combustion Institute, 1969.

10. CLYNE, M. A. A., AND THRUSH, B. A.: Proc. Roy. Soc. (London), A275, 544 (1963).

11. KAUFMAN, F., AND DEL GRECO, F. P.: Ninth Symposium (International) on Combustion, p. 659, Academic Press, New York, 1963.

12. WESTENBERG, A. A., AND DE HAAS, N.: J. Chem. Phys. 50, 2512 (1969).

13. GREINER, N. R.: J. Chem. Phys. <u>51</u>, 5049 (1969).

14. WONG, E. L., AND BELLES, F. E.: <u>Activation Energies for Reactions of</u> <u>Hydroxyl Radicals With Hydrogen and Carbon Monoxide</u>, NASA TN D-5507, 1970.

15. SULZMANN, K. G. P., MYERS, B. F., AND BARTLE, E. R.: J. Chem. Phys. <u>42</u>, 3969 (1965).

16. CLARK, T. C., GARNETT, S. H., AND KISTIAKOWSKY, G. B.: J. Chem. Phys. <u>51</u>, 2885 (1969).

TABLE I. Mixture Compositions and Growth Constant Sensitivities

Mixture #	1	2	3	5
Reaction	$OH + H_2 \rightarrow$ $H_2O + H$	$H + O_2 \rightarrow$ $OH + O$	$O + H_2 \rightarrow$ $OH + H$	$OH + CO \rightarrow$ $CO_2 + H$
Composition				
% H_2	0.21	5	0.1046	0.1035
CO	0.11	6	10.0	6.01
O_2	10.0	0.5	0.503	10.0
CO_2	5.0	---	4.99	5.0
Sensitivities				
$\partial \ln \lambda / \partial \ln \nu_1$	0.34	0.01	0.00	0.07
$\partial \ln \lambda / \partial \ln \nu_2$	.33	1.00	.64	.21
$\partial \ln \lambda / \partial \ln \nu_3$	.48	.06	.39	.49
$\partial \ln \lambda / \partial \ln \nu_4$	-.17	-.07	-.06	-.06
$\partial \ln \lambda / \partial \ln \nu_5$	.02	.00	.04	.29

TABLE II. Experimental Results for Mixture 2 and Rate Constants for

$$H + O_2 \longrightarrow OH + O$$

T $^\circ$K	P(Atm)	λ sec^{-1}	k_2 (cm^{3}mole^{-1}sec^{-1})
1166	1.248	1.16×10^4	1.14×10^{11}
1176	1.614	1.37	1.12
1180	1.444	1.26	1.12
1216	1.488	1.67	1.42
1239	1.141	1.39	1.48
1246	1.335	2.03	1.87
1286	1.197	2.50	2.58
1292	1.203	2.44	2.50
1310	1.412	2.66	2.38
1344	1.255	2.71	2.75
1369	1.275	3.19	3.23
1393	1.517	3.60	3.13
1409	1.538	4.07	3.53

TABLE III. Experimental Results for Mixture 3 and Rate Constants for

$$O + H_2 \longrightarrow OH + H$$

T $^\circ$K	P(Atm)	λ sec^{-1}	k_3 (cm^{3}mole^{-1}sec^{-1})
1172	1.383	.548x10^4	4.71x10^{11}
1212	1.435	.696	4.99
1250	1.271	.755	5.33
1255	1.480	.929	6.32
1266	1.492	1.05	7.64
1272	1.509	1.01	6.40
1297	1.106	.910	7.97
1315	1.349	1.08	6.88
1327	1.366	1.09	6.32
1335	1.586	1.28	6.59
1353	1.277	1.21	8.08
1360	1.406	1.23	6.50
1422	1.234	1.32	7.45
1436	1.258	1.43	8.20
1454	1.273	1.44	7.47
1498	1.310	1.68	8.52
1504	1.312	2.17	16.03
1543	1.088	1.77	12.63
1575	1.125	2.12	16.72
1612	1.146	2.21	15.64

TABLE IV. Experimental Results for Mixture 1 and Rate Constants for

$$OH + H_2 \longrightarrow H_2O + H$$

T $^{\circ}$K	P(ATM)	λ sec^{-1}	k_1(cm^{3}mole^{-1}sec^{-1})
1083	1.405	.828x10^4	2.48x10^{12}
1115	1.461	1.36	4.87
1117	1.458	1.41	5.36
1130	1.290	1.22	1.63
1152	1.420	1.36	1.22
1170	1.345	2.08	4.14
1180	1.558	2.20	3.11
1186	1.373	1.66	1.29
1195	1.183	1.62	1.36
1242	1.451	2.33	1.54
1280	1.500	3.10	2.25
1284	1.286	2.99	2.71
1285	1.285	3.10	3.01
1344	1.254	3.66	3.29
1353	1.380	3.40	2.07
1370	1.391	4.19	3.23
1422	1.341	4.55	3.41
1444	1.239	3.98	2.64
1454	1.133	4.34	3.93
1472	1.265	4.96	4.04
1511	1.056	4.50	4.25
1533	1.074	4.70	4.31
1554	1.097	4.57	3.62
1573	1.108	5.65	5.75
1596	1.130	5.36	4.56
1596	1.127	5.91	5.86

TABLE V. Experimental Results for Mixture 5 and Rate Constants for

$$OH + CO \longrightarrow CO_2 + H$$

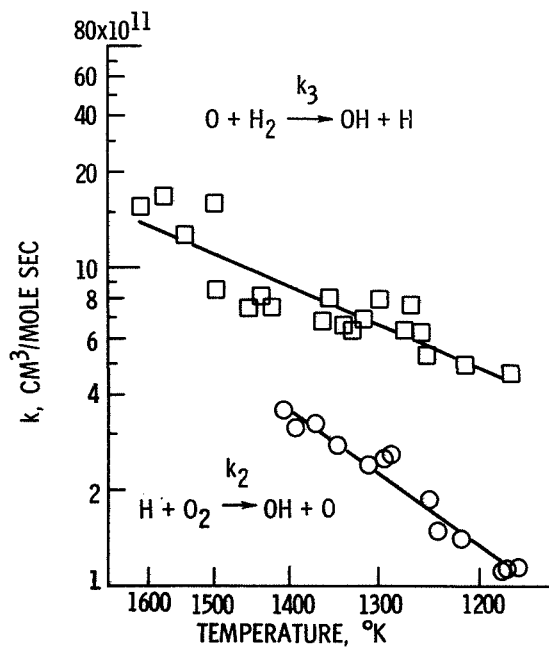| T °K	P(Atm)	$\lambda \, sec^{-1}$	$k_5 \, (cm^3 mole^{-1} sec^{-1})$
1297	1.121	2.63×10^4	2.31×10^{11}
1342	1.170	3.07	2.07
1369	1.204	3.79	3.46
1372	1.211	3.50	2.27
1445	1.537	4.95	2.12
1521	1.373	5.91	3.54
1535	1.383	5.64	2.69
1626	1.189	6.78	5.52
1777	1.000	5.83	3.70
1843	1.039	6.52	4.10
1896	.897	5.63	3.73
1899	1.076	5.85	2.41

Figure 1. - Rate constants for reactions II
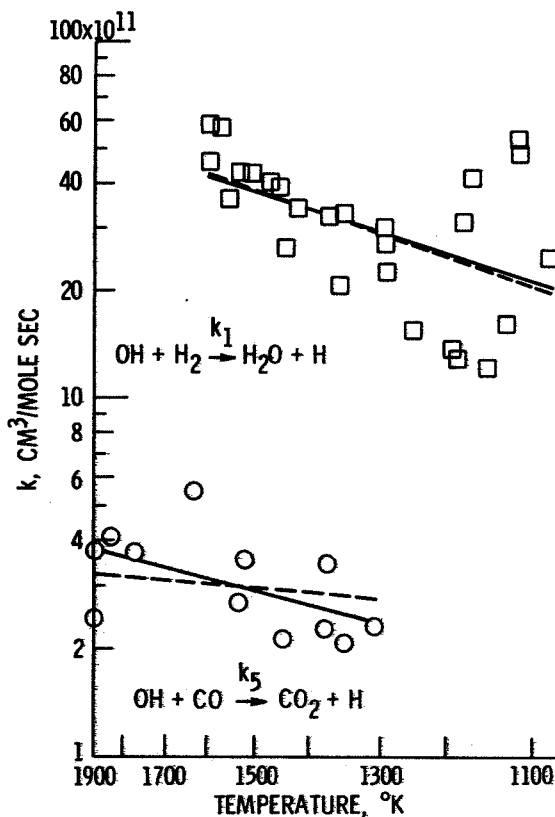and III. Solid lines-least squares fit to
experimental data.

Figure 2. - Rate constants for reactions I and
V. Solid lines-least squares fit to experi-
mental data. Dashed lines-least squares fit
to experimental data plus 300° K datum of
Greiner[13].