

# SHOCK-TUBE MEASUREMENTS OF SPECIFIC REACTION RATES IN THE BRANCHED-CHAIN H<sub>2</sub>-CO-O<sub>2</sub> SYSTEM

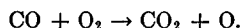
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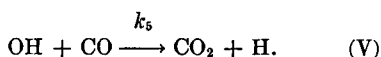
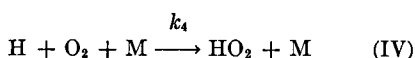
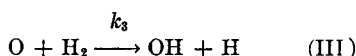
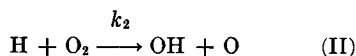
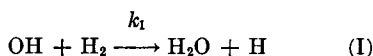
Rate constants of four elementary bimolecular reactions have been determined by monitoring the exponential growth of CO flame band emission behind incident shocks in four suitably chosen gas mixtures. Results are as follows: OH + H<sub>2</sub> → H<sub>2</sub>O + H,  $k_1 = 2.1 \times 10^{13} \exp(-5.1 \text{ kcal}/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$  (1100°–1600°K); H + O<sub>2</sub> → OH + O,  $k_2 = 1.25 \times 10^{14} \exp(-16.3 \text{ kcal}/RT)$  (1150°–1400°K); O + H<sub>2</sub> → OH + H,  $k_3 = 2.96 \times 10^{13} \exp(-9.8 \text{ kcal}/RT)$  (1200°–1600°K); and OH + CO → CO<sub>2</sub> + H,  $k_5 = 4.2 \times 10^{11} \times \exp(-1.0 \text{ kcal}/RT)$  (1300°–1900°K). Less directly, by analysis of early, linear luminosity and times to 50 percent of peak light intensity, the rate of the initiation reaction, CO + O<sub>2</sub> → CO<sub>2</sub> + O is estimated to be  $k_4 = 1.6 \times 10^{13} \exp(-41 \text{ kcal}/RT)$ .

## 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



These concentrations may then grow exponentially via the well-known branched-chain scheme,



Theory shows<sup>1,2</sup> that the oxygen-atom concentration increases as  $[\text{O}] \simeq A \exp \lambda t$  (except very early in the reaction), where  $\lambda$  is the positive root of the cubic equation

$$\begin{aligned} \lambda^3 + (\nu_1 + \nu_2 + \nu_3 + \nu_4 + \nu_5)\lambda^2 \\ + [(\nu_1 + \nu_5)(\nu_3 + \nu_4) + \nu_3\nu_4]\lambda \\ - \nu_3(\nu_1 + \nu_5)(2\nu_2 - \nu_4) = 0. \end{aligned} \quad (1)$$

Here  $\nu_1 \equiv k_1[\text{H}_2]$ ,  $\nu_2 \equiv k_2[\text{O}_2]$ ,  $\nu_3 \equiv k_3[\text{H}_2]$ ,  $\nu_4 \equiv k_4[\text{O}_2][\text{M}]$ , and  $\nu_5 \equiv k_5[\text{CO}]$ . Thus the exponential growth constant  $\lambda$  depends upon 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<sup>3</sup> 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.<sup>4</sup>

Gas mixtures contained varying amounts of H<sub>2</sub>, CO, O<sub>2</sub>, and in some mixtures CO<sub>2</sub> 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<sup>4</sup> 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 Ref. 4. In general, the extent of chemical reaction was small and changes in gas properties were brought about largely by the gasdynamics 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  $\nu_4$  is generally small in comparison with the other  $\nu$  and can be neglected for purposes of a qualitative discussion. Second,  $\lambda$  turns out to be a small positive root—of the order of the smaller  $\nu$  values and small compared with the larger  $\nu$  values. Thus, we neglect  $\lambda^3$  in comparison with the other terms and rewrite Eq. (1)

$$[(\nu_1 + \nu_5) + \nu_2 + \nu_3]\lambda^2 + \nu_3(\nu_1 + \nu_5)\lambda \simeq 2\nu_2\nu_3(\nu_1 + \nu_5). \quad (2)$$

If the amount of hydrogen in a mixture is large in comparison to oxygen,  $\nu_1$  and  $\nu_3$  are large and the term involving  $\lambda^2$  may be neglected; in this event

$$\lambda \simeq 2\nu_2. \quad (3)$$

On the other hand, if only a trace of hydrogen is present,  $\nu_3$  is small, the term involving  $\lambda$  may be neglected, and

$$\lambda^2 \simeq 2\nu_2\nu_3(\nu_1 + \nu_5)/[\nu_2 + (\nu_1 + \nu_5)]. \quad (4)$$

If we choose a mixture with a large amount of carbon monoxide,  $\nu_5$  is large and

$$\lambda \sim (2\nu_2\nu_3)^{1/2}, \quad (5)$$

whereas if there is a large amount of oxygen,  $\nu_2$  is

large and

$$\begin{aligned} \lambda &\sim [2\nu_3(\nu_1 + \nu_5)]^{1/2} \\ &\rightarrow (2\nu_3\nu_1)^{1/2} \quad [\text{H}_2] > [\text{CO}] \\ &\rightarrow (2\nu_3\nu_5)^{1/2} \quad [\text{CO}] > [\text{H}_2]. \end{aligned} \quad (6)$$

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 foregoing 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 differentiation of Eq. (1). For example,

$$\begin{aligned} (\partial \ln \lambda / \partial \ln \nu_3) &= \frac{1}{2} \\ &- \frac{1}{2} \{ [\lambda^2 + 2\nu_3\lambda + (\nu_1 + \nu_5)(\nu_3 - \nu_4) \\ &+ \nu_3\nu_4] / [3\lambda^2 + 2(\nu_1 + \nu_2 + \nu_3 + \nu_4 + \nu_5)\lambda \\ &+ (\nu_1 + \nu_5)(\nu_3 + \nu_4) + \nu_3\nu_4] \}. \end{aligned} \quad (7)$$

Equation (7) shows the growth constant will depend upon something less than the square root of  $\nu_3$ —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 1 atm 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 ( $5 \times 10^3$  to  $7 \times 10^4 \text{ sec}^{-1}$ ), and 4) 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

TABLE I  
Mixture compositions and growth constant sensitivities

	Mixture No.			
	1	2	3	5
Reaction	OH + H <sub>2</sub> → H <sub>2</sub> O + H	H + O <sub>2</sub> → OH + O	O + H <sub>2</sub> → OH + H	OH + CO → CO <sub>2</sub> + H
Composition, %:				
H <sub>2</sub>	0.21	5	0.1046	0.1035
CO	0.11	6	10.0	6.01
O <sub>2</sub>	10.0	0.5	0.503	10.0
CO <sub>2</sub>	5.0	—	4.99	5.0
Sensitivities:				
$\partial \ln \lambda / \partial \ln \nu_1$	0.34	0.01	0.00	0.07
$\partial \ln \lambda / \partial \ln \nu_2$	0.33	1.00	0.64	0.21
$\partial \ln \lambda / \partial \ln \nu_3$	0.48	0.06	0.39	0.49
$\partial \ln \lambda / \partial \ln \nu_4$	-0.17	-0.07	-0.06	-0.06
$\partial \ln \lambda / \partial \ln \nu_5$	0.02	0.00	0.04	0.29

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<sub>2</sub>, carbon monoxide was not relaxed and rate constants gave an activation energy of 15 kcal for Reaction (III), much higher than literature values.<sup>5</sup> Results from Mixture 3, with added CO<sub>2</sub>, 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 upon  $k_2$  and are only slightly affected by the rates of the other reactions (see Table I). Values of  $\nu_4$  were calculated from the  $k_4$  suggested by the Leeds Group.<sup>6</sup> Trial values of  $k_1$ ,  $k_3$ , and  $k_5$  were also taken from the Leeds recommendations,<sup>5-7</sup> but final values were taken from our own determina-

tions. This involves an iterative procedure, since our values of  $k_3$  depend, in turn, upon our values of  $k_2$ , 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  $\lambda$  was measured; during this period the temperature varied by less than 10° and the pressure by less than 1%. Rate constants are plotted versus reciprocal temperature in Fig. 1. The least-squares line through the data is

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

TABLE II

Experimental results for Mixture 2 and rate constants for  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$

$T$ (°K)	$P$ (atm)	$\lambda$ sec <sup>-1</sup>	$k_2$ (cm <sup>3</sup> mole <sup>-1</sup> sec <sup>-1</sup> )
1166	1.248	$1.16 \times 10^4$	$1.14 \times 10^{11}$
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

The standard deviation<sup>8</sup> of  $\ln k_2$  is  $\pm 0.094$ , or about 10%; the standard deviation<sup>8</sup> of the activation energy is 1.1 kcal. Rates given by Eq. (8) fall somewhat below most previous high-temperature ( $T > 1000^\circ\text{K}$ ) determinations and, as a consequence, lie about 30% below the recommendation of the Leeds group,<sup>6</sup> but well within their suggested error limit of  $\pm 50\%$ . The activa-

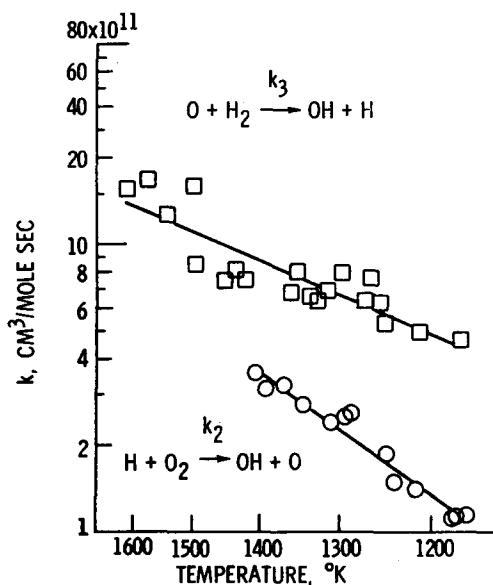


FIG. 1. Rate constants for Reactions (II) and (III). Solid lines: least-squares fit to experimental data.

tion energy of 16.3 kcal is slightly more than the endothermicity of Reaction (II), 16.15 kcal at 1300°K, in contrast to several other recent shock-tube studies<sup>6,9</sup> 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<sup>10</sup> and Kaufman and Del Greco.<sup>11</sup>

It should be emphasized that these satisfying results are obtained only when the effects of

TABLE III

Experimental results for Mixture 3 and rate constants for  $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$

$T$ (°K)	$P$ (atm)	$\lambda$ sec <sup>-1</sup>	$k_3$ (cm <sup>3</sup> mole <sup>-1</sup> sec <sup>-1</sup> )
1172	1.383	$0.548 \times 10^4$	$4.71 \times 10^{11}$
1212	1.435	0.696	4.99
1250	1.271	0.755	5.33
1255	1.480	0.929	6.32
1266	1.492	1.05	7.64
1272	1.509	1.01	6.40
1297	1.106	0.910	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

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% larger with an apparent activation energy of only 11.9 kcal.

Rate constants for Reaction (III) are shown in Table III are also plotted in Fig. 1. The least-squares line through the data is

$$k_3 = 2.96 \times 10^{13}$$

$$\times \exp(-9.8 \text{ kcal}/RT) \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}. \quad (9)$$

The standard deviation of  $\ln k_3$  is  $\pm 0.184$ , or

about 20%; 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 upon 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<sup>5</sup>; they are about 50% above the Leeds recommendation<sup>5</sup> which is somewhat outside their suggested error limit of  $\pm 30\%$ . (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% above an extrapolation of the more recent data of Westenberg and de Haas.<sup>12</sup> 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.<sup>5</sup>

TABLE IV

Experimental results for Mixture 1 and rate constants for  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$

$T$ (°K)	$P$ (atm)	$\lambda$ sec <sup>-1</sup>	$k_1$ (cm <sup>3</sup> mole <sup>-1</sup> sec <sup>-1</sup> )
1083	1.405	$0.828 \times 10^4$	$2.48 \times 10^{12}$
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

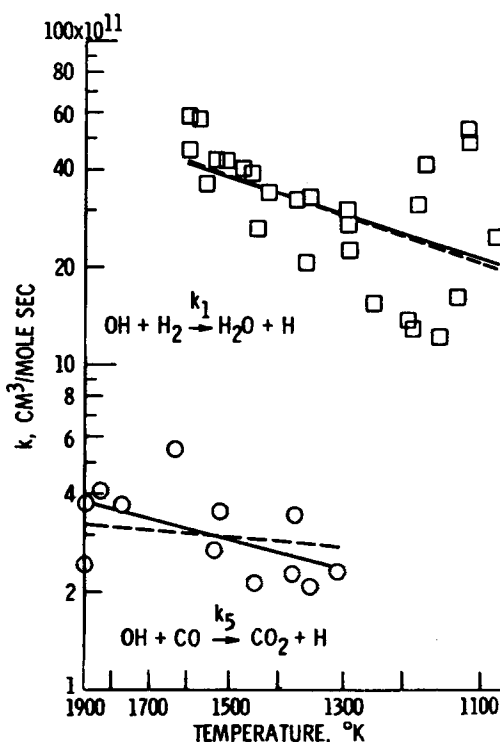


FIG. 2. Rate constants for Reactions (I) and (V). Solid lines: least-squares fit to experimental data. Dashed lines: least-squares fit to experimental data plus 300°K datum of Greiner (Ref. 13).

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

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

The standard deviation of  $\ln k_1$  is  $\pm 0.41$ , or about 40%; 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.<sup>5</sup> 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% 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.<sup>13</sup> This gives

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

TABLE V

Experimental results for Mixture 5 and rate constants for  $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$

$T$ ( $^{\circ}\text{K}$ )	$P$ (atm)	$\lambda$ sec $^{-1}$	$k_5$ (cm $^3$ mole $^{-1}$ sec $^{-1}$ )
1297	1.121	$2.63 \times 10^4$	$2.31 \times 10^{11}$
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

The standard deviation of  $\ln k_1$  remains  $\pm 0.41$ , 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% 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

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

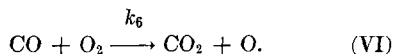
The standard deviation of  $\ln k_5$  is  $\pm 0.28$ , or about 30%; the standard deviation of the activation energy is 1.9 kcal. In the temperature range of 1300 $^{\circ}$ –1900 $^{\circ}$ K, Eq. (12) gives rate constants 10–35% below the Leeds recommendation.<sup>7</sup> The 3.7 kcal activation energy is almost certainly too large; recent low-temperature studies<sup>13,14</sup> suggest 0.2–1.0 kcal. By including in the least-squares analysis Greiner's<sup>13</sup> recent 300 $^{\circ}$ K value,  $k_5 = 8.6 \times 10^{10}$ , we obtain

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

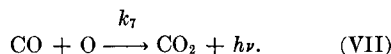
The standard deviation of  $\ln k_5$  remains about the same,  $\pm 0.29$ , but the standard deviation of the activation energy is only 0.2 kcal. Equation (13) is shown as a dashed line in Fig. 2. To the eye, Eq. (13) seems almost as good a representation

of the data as Eq. (12). In the experimental temperature range, Eqs. (12) and (13) differ by at most 15%. 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



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,



the increase of light emission with time is

$$dI/dt \propto k_6 k_7 [\text{CO}]^2 [\text{O}_2]. \quad (14)$$

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,<sup>7</sup>  $E_6 = 41$  kcal. This is less than the 48–51 kcal activation energy inferred<sup>2,15</sup> from the data of Sulzmann, Myers, and Bartle,<sup>15</sup> but larger than the  $29 \pm 11$  kcal derivable from a recent determination<sup>16</sup> 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 upon 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 pre-exponential factor in the Arrhenius equation so as to fit observed times to 50% peak

light intensity. In this fashion, we obtain

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

with a standard deviation in  $\ln k_6$  of  $\pm 0.54$ , which is a factor of 1.7. This is more than an order-of-magnitude larger than previous estimates<sup>2,15</sup> of this rate. On the other hand, if we used Eq. (15) to calculate the rate of the reverse of Reaction (VI) at 3000°K, we obtain a rate only 30% below the recent measurements of Clark, Garnett, and Kistiakowsky.<sup>16</sup>

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; it is 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  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$  and  $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$ . 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  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$  and  $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$  are less precise but are perhaps the most direct determinations of these rates for temperatures above 1100°K (previous high temperature determinations of these rates have been based on flame sampling). Finally, we have estimated the rate of the initiation reaction  $\text{CO} + \text{O}_2 \rightarrow \text{CO}_2 + \text{O}$ .

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### COMMENTS

G. L. Schott and R. W. Getzinger, *Los Alamos Scientific Laboratory*. Do the rate coefficient parameters determined in this investigation provide a satisfactory description of the exponential growth constants found previously<sup>1,2</sup> by the same CO-O radiative association method in the ignition of  $\text{H}_2$ -CO- $\text{O}_2$ -Ar mixtures, but at more nearly stoichiometrically balanced compositions ( $\text{H}_2:\text{O}_2 \approx 1$ ;  $\text{CO}:\text{H}_2 \approx 5$ ), over a higher

range of temperatures, and in nonflowing gases behind reflected shock waves? How close is the agreement, or how serious the disagreement?

#### References

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*Authors' Reply.* Our rate constants predict exponential growth constants somewhat smaller than those observed by Gutman, Schott, et al. (This is not surprising, since they infer values of  $k_2$  20%–30% larger than ours.) For example, for the mixture  $H_2 = O_2 = 0.49\%$ ,  $CO = 3.22\%$ , we predict a growth constant 18%–24% smaller than the smoothed values of Gutman and Schott, *J. Chem. Phys.* 46, 4576 (1967); for the mixtures reported by Schott at the 12th Symposium, p. 569, discrepancies were larger: Mixture I, –15%; Mixture II, –20% to –30%; and Mixture III, –25% to –35%.

K. P. G. Sulzmann, *University of California at San Diego*. (a) How good is the approximation obtained by linearizing the kinetic equations in the concentration of the chain carriers for your present data analysis and for the analysis you did for our (Sulzmann–Myers–Bartle) data published in *J. Chem. Phys.* 42, 3969 (1965) and 43, 1220 (1965)?

(b) Can you ignore the temperature changes in your mixtures during the induction regime in your present analysis?

(c) Would inclusion of the reaction  $CO + O + M \rightarrow CO_2 + M$  decrease your value for the rate coefficient of the reaction  $CO + O_2 \rightarrow CO_2 + O$  to our and Kistiakowsky's new expression?

*Authors' Reply.* (a) In conjunction with our boundary-layer analysis, we used a computer program which integrated a more-extensive scheme of reactions. Thus, the effects of depletion of reactants and recombination reactions were considered. These computations show that the linearized analysis is valid in the time scale of our experimental observations.

(b) Temperature changes due to boundary-layer growth (as well as density and residence time changes) were important and were taken into account. The computer program also considers temperature changes due to chemical reaction, but such changes were always very small.

(c) The reaction  $CO + O + M \rightarrow CO_2 + M$  was included in our numerical computations. At early times (where we used the linear buildup of radiation to estimate the activation energy of the

initiation step), the rate of this recombination reaction is slow in comparison to the initiation reaction. [It is also slower than Reactions (II) and (III), which create and destroy oxygen atoms.] Since the reaction was included in the numerical computations, any effects on the time to half-peak luminosity (which we used to estimate the absolute values of the initiation rate) have been taken into account.

The discordant values for the rate of the initiation reaction  $CO + O_2 \rightarrow CO_2 + O$  are a cause for concern. We took special pains to ensure rapid vibrational relaxation of carbon monoxide and it is possible that some of the very much slower rates observed by others may be appropriate for carbon monoxide that is vibrationally cold.

F. Kaufman, *University of Pittsburgh*. In reaction mixtures containing much  $H_2$ , need one not also consider the initiation reaction  $H_2 + O_2 \rightarrow HO_2 + H$ ?

*Authors' Reply.* Baldwin et al. [*Trans. Faraday Soc.* 63, 1676 (1967)] suggest that the rate of the reaction  $H + HO_2 \rightarrow 2 OH$  is about  $7 \times 10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$  at 773°K. Clyne and Thrush [*Proc. Roy. Soc. (London)* A275, 559 (1963)] suggest that the rate of the reaction  $H + HO_2 \rightarrow H_2 + O_2$  is about one-third of the reaction to form hydroxyl, which would be  $2.3 \times 10^{13}$ . This is a rapid reaction, perhaps a tenth of collision frequency, so there can be little activation energy. From detailed balancing, and assuming that the activation energy is simply the endothermicity, we estimate the rate constant for the initiation reaction  $H_2 + O_2 \rightarrow H + HO_2$  to be  $5 \times 10^{13} \exp(-57 \text{ kcal}/RT)$ . In our richest mixture (Mixture 2) at 1400°K, the rate of this initiation process would be one-hundredth the rate due to  $CO + O_2 \rightarrow CO_2 + O$ .

However, we should again emphasize that there is considerable uncertainty in our estimate of the initiation rate. Belles and Brabbs (This Symposium) have obtained an initiation rate for Mixture 2; if initiation in their mixture is ascribed to  $CO + O_2 \rightarrow CO_2 + O$ , the rate of this reaction would be  $2.6 \times 10^{12} \exp(-41 \text{ kcal}/RT)$  (assuming our activation energy is correct). This is only about one-sixth as fast as Eq. (15), but nonetheless still sixty times as fast as my estimate of the rate of  $H_2 + O_2 \rightarrow H + HO_2$  at their temperature, 1140°K.