ShockTube Study of the Recombination Rate of Hydrogen Atoms with Oxygen Molecules

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Shock-Tube Study of the Recombination Rate of Hydrogen Atoms with Oxygen Molecules*

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Measurements have been made of the rate of chain branching during the induction period of the H_2-O_2 reaction. Mixtures of H_2-O_2-CO-Ar were shock heated and the "blue continuum" emission from the $O + CO \rightarrow CO_2 + h\nu$ reaction was monitored using an end-on technique for sensitivity. Experiments performed at different densities were analyzed to yield the rate coefficient $k_4^{Ar} = 3.3 \times 10^9$ liters^2 mole^{-2}·sec^{-1} at 1100°K for the reaction

$$H + O_2 + Ar \xrightarrow{k_4^{Ar}} HO_2 + Ar.$$
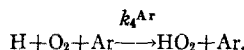
This value when combined with other literature values for k_4^{Ar} yields the temperature-dependent expressions $k_4^{Ar} = (2.00 \pm 0.25) \times 10^9 [\exp(870 \pm 70 \ cal/RT)]$ liter^2 mole^{-2}·sec^{-1} and $k_4^{Ar} = (1.5 \pm 0.7) \times 10^{12} T^{-0.88 \pm 0.08}$ liter^2 mole^{-2}·sec^{-1}. In addition values of k_1 for the reaction

$$H + O_2 \xrightarrow{k_1} OH + O$$
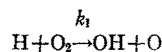
were obtained from the data between 975° and 2060°K and combined in the Arrhenius expression $k_1 = 9.54 \times 10^{10} \exp(-14.7 \ kcal/RT)$ liters mole^{-1}·sec^{-1} accurate to $\pm 20\%$ over our range. A value for $k_2 = 1.98 \times 10^9$ liters mole^{-1}·sec^{-1} ($\pm 40\%$) at 1500°K was obtained for the reaction
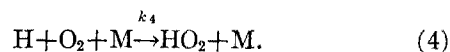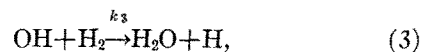
$$O + H_2 \xrightarrow{k_2} OH + H.$$
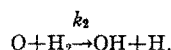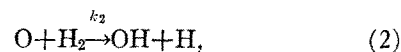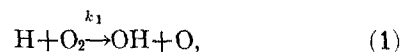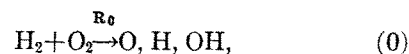
The end-on technique is shown to be a useful tool to study recombination reactions involving only one free radical.

INTRODUCTION

The reaction $H + O_2 + M \rightarrow HO_2 + M$ is an important radical recombination step in many gaseous oxidation reactions and plays a particularly vital role as a chain-terminating process at the second limit of the H_2-O_2 reaction. In this study we have determined the rate of this reaction for $M = Ar$ (k_4^{Ar}) in the temperature range 1018°–1285°K. The purpose of this study was twofold: first, to obtain an accurate value for this constant to be used in the analysis of future shock-tube studies of the kinetics of the hydroperoxyl radical and, second, to assess the potential of the "end-on" shock-tube technique for studying recombination reactions. Our experiments consisted of shock heating H_2-O_2-CO-Ar mixtures and subsequently monitoring the exponential growth of the O-atom concentration during the induction period of this reaction. Values for k_4^{Ar} were obtained from the chain-branching equation using the measured exponential growth constants.

When mixtures of H_2 and O_2 are suddenly heated, a short induction period is observed during which there is a negligible depletion of reactants and an exponential rise in the concentration of the chain carriers (e.g., $[O] = [O]_0 e^{\alpha t}$) at essentially constant temperature and pressure. The significant reactions during this period are[1]

$$H_2 + O_2 \xrightarrow{R_0} O, H, OH, \tag{0}$$

$$H + O_2 \xrightarrow{k_1} OH + O, \tag{1}$$

$$O + H_2 \xrightarrow{k_2} OH + H, \tag{2}$$

$$OH + H_2 \xrightarrow{k_3} H_2O + H, \tag{3}$$

$$H + O_2 + M \xrightarrow{k_4} HO_2 + M. \tag{4}$$

Kondratiev[1] and others[2-5] have shown that the exponential growth constant α is the positive root of the

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[1] V. N. Kondratiev, *Kinetika Ximitcheshix Gasovix Reaktsii* (USSR Academy of Sciences, Moscow, 1958), Sec. 38 [English transl.: *Chemical Kinetics of Gas Reactions* (Pergamon Press, Inc., 1964), Sec. 39].

[2] R. S. Brokaw, Symp. Combust. 10th Univ. Cambridge, Cambridge, England, 1964, 269 (1965).

[3] F. E. Belles and M. R. Lauver, Symp. Combust. 10th Univ. Cambridge, Cambridge, England, 1964, 285 (1965).

[4] D. L. Ripley and W. C. Gardiner, Jr., J. Chem. Phys. **44**, 2285 (1966).

[5] T. Asaba, W. C. Gardiner, Jr., and R. F. Stubbeman, Symp. Combust. 10th Univ. of Cambridge, Cambridge, England, 1964, 295 (1965).

equation,

$$\alpha^3 + (K_1 + K_2 + K_3 + K_4[M])\alpha^2$$
$$+ (K_2K_3 + K_2K_4[M] + K_3K_4[M])\alpha$$
$$+ (K_2K_3K_4[M] - 2K_1K_2K_3) = 0, \quad (I)$$

where

$$K_1 = k_1[O_2], \qquad K_2 = k_2[H_2],$$
$$K_3 = k_3[H_2] \quad \text{and} \quad K_4 = k_4[O_2].$$

Values for k_1 and k_2 were obtained from Eq. (I), using data from low-density experiments where Reaction (4) has a minor role. Values for k_4 were obtained by solving Eq. (I), using these values for k_1 and k_2, literature values for k_3, and experimentally determined growth constants from high-density experiments.

All bimolecular rate constants reported in this paper are in units of liters mole^{-1}·seconds^{-1}, and termolecular rate constants are in units of liters^2 mole^{-2}·second^{-1}.

EXPERIMENTAL

In order to measure the exponential growth of the O-atom concentration during the induction period, H_2–O_2–CO–Ar mixtures were shock-heated and the chemiluminescent emission from the reaction $O + CO \rightarrow CO_2 + h\nu$ was monitored. Since the emission intensity is proportional to $[CO][O]$[6,7] and since the concentration of CO was constant during the induction period, the emission exhibited the same exponential growth as the O-atoms. To obtain sufficient intensity for our induction-period measurements, we used the special end-on technique described in a previous paper[8] (hereafter designated as GS), in which we studied the reaction behind the reflected shock wave by monitoring the total light emitted axially through a 7.6-cm-diam window mounted in the end flange of the shock tube. As long as all the gas behind the reflected shock wave is still in the induction period, the total integrated light intensity observed by this technique is given by $I = I_0(e^{\alpha t} - 1 - \alpha t)$, where I_0 is constant in each experiment and t is the laboratory time after shock reflection. As soon as $e^{\alpha t} \gg \alpha t$ (typically for $t > 35\mu$sec), the integrated emission signal rises exponentially with the same time constant as that for the free-radical growth. A sample oscillogram is shown in Fig. 1.

The apparatus and experimental techniques were similar to those described in GS and therefore are only summarized here. The 10-cm-diam stainless-steel shock tube used in this study has a 3.96-m-long test section and a 1.82-m-long driver section. Four thin film heat gauges used to measure the shock velocity are mounted 25.4 cm apart along the tube, the last one located 8.0
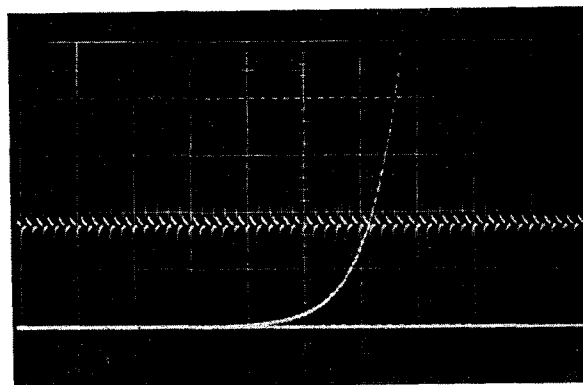

FIG. 1. Oscillogram from typical experiment. 0.50% H_2, 1.50% O_2, 3.0% CO, 95% Ar; $T = 1135°$K, $[M] = 2.34 \times 10^{-2}$ moles/liter. 545 scope, CA preamp; vertical sensitivity, 200 mV/div; horizontal sweep rate, 50 μ sec/div; 10-μ sec timing marks on oscillogram.

cm from the end of the shock tube. Signals from these gauges are mixed with 1-μsec time marks and displayed on a Tektronix 535 A oscilloscope modified for faster display. This scope is triggered by the signal from a laser–schlieren[9] station located 25.4 cm upstream from the first heat gauge. The 0.3-mW beam from an Optics Technology Model 170 He–Ne gas laser is aligned normal to the axis of the tube, traverses the tube through two small windows, and is centered on a knife edge located 27 cm from the shock tube. Deflection due to passage of the shock front through the beam is detected by an RCA 931-A photomultiplier placed behind the knife edge. The shock velocity at the end of the tube was obtained from extrapolation of the data from the four thin film gauges. Hugoniot calculations for conditions of no chemical reactions behind both incident and reflected shock waves were used to determine the temperature and concentration conditions in each experiment. Thermodynamic data for the reactants was taken from the JANAF Tables.[10]

The end flange of the shock tube was fitted with a 10-cm-diam and 1.25-cm-thick Pyrex glass disk, masked on the outside to provide a 7.6-cm-diam axial window. A plano–convex lens (focal length 57.1 cm, diameter 8.6 cm) located 3 cm behind the window focused the light which is emitted parallel to the axis of the shock tube onto a telecentric aperture 1.9 cm in diameter located at the focal point. The light intensity was recorded by an Amperex 150 AVP photomultiplier tube (S-11 response) located behind the aperture. The output of the tube was fed to a cathode follower and then directed to a Tektronix 545 oscilloscope (CA preamplifier) fitted with a Polaroid camera. A thin film heat gauge deposited on the end window provided a signal that triggered a single sweep of the oscilloscope upon arrival of the shock wave at the end of the tube.

[6] W. E. Kasan, Combust. Flame **3**, 39 (1959).

[7] M. A. A. Clyne and B. A. Thrush, Proc. Roy. Soc. (London) A269, 404 (1962).

[8] D. Gutman and G. L. Schott, J. Chem. Phys. **46**, 4576 (1967).

[9] J. H. Kiefer and R. W. Lutz, J. Chem. Phys. **44**, 658 (1966).

[10] *JANAF Thermochemical Tables*, D. K. Stull, Ed. (The Dow Chemical Co., Midland, Mich., 1965).

TABLE I. Experimental results of induction-period emission experiments.

$\alpha\times10^{-5}$ (sec⁻¹)	$[M]\times10^2$ (mole/liter)	$\alpha/2[O_2]\times10^{-8}$ (liter/mole·sec)	T (°K)	$\alpha\times10^{-5}$ (sec⁻¹)	$[M]\times10^2$ (mole/liter)	$\alpha/2[O_2]\times10^{-8}$ (liter/mole·sec)	T (°K)
$X_{H_2}=0.0050$, $X_{O_2}=0.015$, $X_{CO}=0.030$, $X_{Ar}=0.950$				$X_{H_2}=0.0050$, $X_{O_2}=0.015$, $X_{CO}=0.030$, $X_{Ar}=0.950$			
(Low density)				0.353	2.12	0.556	1155
				0.332	2.17	0.510	1155
0.168	0.156	3.59	1642	0.329	2.44	0.450	1140
0.201	0.187	3.65	1580	0.362	2.34	0.515	1135
0.209	0.291	2.90	1530	0.386	2.28	0.568	1125
0.205	0.292	2.34	1452	0.299	2.48	0.404	1125
0.177	0.261	2.26	1430	0.368	2.37	0.518	1115
0.189	0.312	2.01	1385	0.210	2.26	0.310	1080
0.174	0.281	2.06	1367	0.250	2.44	0.341	1080
0.187	0.334	1.86	1350	0.166	2.38	0.232	1040
0.163	0.359	1.52	1320	0.111	2.48	0.151	1030
0.187	0.382	1.63	1295	0.124	2.35	0.176	1025
0.160	0.407	1.31	1290	0.119	2.48	0.160	1017
0.153	0.426	1.20	1250				
0.157	0.497	1.05	1218	(High density)			
0.122	0.464	0.903	1195				
0.120	0.437	0.903	1185	3.74	3.72	3.36	1670
0.136	0.512	0.883	1180	3.63	3.83	3.15	1610
0.138	0.554	0.829	1155	3.63	4.03	3.01	1610
0.126	0.576	0.727	1145	3.17	4.06	2.60	1510
0.122	0.597	0.676	1137	2.86	4.20	2.27	1485
0.124	0.616	0.671	1122	2.37	4.63	1.71	1455
0.109	0.636	0.571	1110	2.32	4.49	1.72	1445
0.107	0.656	0.546	1100	2.05	4.61	1.49	1395
0.112	0.680	0.547	1100	2.95	4.71	1.38	1385
0.106	0.730	0.485	1100	1.70	4.80	1.18	1345
0.0970	0.766	0.422	1080	1.65	4.97	1.11	1345
0.0917	0.688	0.444	1067	1.42	4.98	0.946	1285
0.0900	0.665	0.385	1052	1.48	5.10	0.968	1285
0.0776	0.852	0.304	1023	1.16	5.27	0.735	1285
0.0703	0.826	0.284	1017	0.952	5.44	0.606	1220
0.0705	0.795	0.295	1004	0.800	5.24	0.487	1195
0.0700	0.884	0.264	1004	0.694	5.56	0.416	1175
0.0641	0.767	0.279	995	0.559	5.71	0.327	1165
0.0663	0.899	0.246	993	0.554	5.62	0.329	1150
0.0614	0.904	0.227	987	0.270	5.75	0.157	1137
0.0606	0.851	0.238	987	0.334	5.96	0.188	1135
				0.210	5.99	0.117	1125
(Medium density)				0.336	5.82	0.193	1122
				0.193	6.09	0.107	1110
2.19	1.09	6.68	1965	0.296	5.86	0.168	1105
2.00	1.13	5.92	1857	0.227	5.85	0.129	1070
2.17	1.20	6.04	1857	1.29[a]	5.08	0.848	1301
1.87	1.18	5.30	1800	1.21[a]	5.23	0.774	1254
1.77	1.30	4.55	1762	1.00[a]	5.35	0.624	1248
1.81	1.69	4.67	1755	0.928[a]	5.58	0.554	1210
1.62	1.34	4.04	1705	0.764[a]	5.61	0.458	1205
1.59	1.38	3.85	1645	0.954[a]	5.33	0.597	1198
1.48	1.41	3.49	1585	1.06[a]	5.35	0.644	1189
1.60	1.47	3.64	1575	0.874[a]	5.48	0.532	1183
1.24	1.51	2.72	1545	0.612[a]	5.71	0.358	1177
1.25	1.51	2.76	1542	0.541[a]	5.74	0.315	1169
1.46	1.57	3.10	1530	0.390[a]	5.97	0.217	1141
1.24	1.62	2.56	1510	0.473[a]	5.84	0.271	1138
1.33	1.66	2.68	1490	0.424[a]	5.78	0.244	1107
0.960	1.63	1.97	1442	0.277[a]	5.98	0.155	1080
1.12	1.68	2.21	1430				
0.979	1.76	1.88	1413	$X_{H_2}=0.0050$ $X_{O_2}=0.005$ $X_{CO}=0.030$ $X_{Ar}=0.960$			
0.900	1.77	1.59	1410	(Medium density)			
1.10	1.84	2.00	1410				
0.850	1.72	1.66	1395	1.44	1.10	13.3	2040
0.822	2.00	1.38	1330	1.48	1.10	13.5	2040
0.798	1.81	1.35	1315	1.40	1.15	12.1	2000
0.795	1.87	1.42	1305	1.38	1.21	11.4	1943
0.828	1.93	1.43	1305	1.15	1.30	8.86	1793
0.670	1.99	1.13	1270	0.980	1.27	7.70	1750
0.688	2.04	1.13	1255	1.01	1.38	7.31	1705
0.562	2.17	0.864	1240	0.728	1.24	5.89	1655
0.614	2.10	0.969	1225	0.836	1.53	5.49	1613
0.503	2.32	0.725	1188	0.920	1.47	6.28	1608
0.458	2.31	0.662	1183				
0.473	2.20	0.717	1177				

TABLE I (Continued)

$\alpha \times 10^{-5}$ (sec^{-1})	$[M]\times 10^2$ (mole/liter)	$\alpha/2[O_2]\times 10^{-8}$ (liter/mole·sec)	T (°K)	$\alpha \times 10^{-5}$ (sec^{-1})	$[M]\times 10^2$ (mole/liter)	$\alpha/2[O_2]\times 10^{-8}$ (liter/mole·sec)	T (°K)
$X_{H_2}=0.0050$	$X_{O_2}=0.005$	$X_{CO}=0.030$	$X_{Ar}=0.960$	$X_{H_2}=0.0050$	$X_{O_2}=0.005$	$X_{CO}=0.030$	$X_{Ar}=0.960$
0.921	1.58	5.82	1600	0.160	2.41	0.673	1100
0.808	1.51	5.35	1577	0.142	2.12	0.670	1100
0.783	1.51	5.18	1576	0.150	2.54	0.592	1060
0.813	1.50	5.43	1555				
0.705	1.65	4.27	1515		(High density)		
0.702	1.74	4.04	1465				
0.562	1.61	3.48	1455	1.04	4.75	2.18	1370
0.606	1.84	3.30	1440	1.07	4.59	2.32	1370
0.511	1.61	3.18	1437	0.885	4.75	1.87	1295
0.527	1.74	3.02	1395	0.561	5.30	1.06	1260
0.434	1.86	2.22	1355	0.522	5.44	0.960	1220
0.418	2.02	2.06	1325	0.338	5.52	0.610	1200
0.391	1.88	2.08	1296	0.404	5.56	0.727	1180
0.339	2.04	2.04	1296	0.268	5.80	0.462	1175
0.359	2.02	1.78	1280	0.383	5.54	0.690	1175
0.333	2.08	1.60	1270	0.295	5.59	0.529	1160
0.250	2.14	1.17	1220	0.198	5.77	0.343	1155
0.240	2.08	1.15	1192	0.163	5.83	0.279	1125
0.206	2.07	1.00	1182	0.113	5.92	0.191	1130
0.218	2.20	0.990	1173	0.832[b]	5.22	1.59	1286
0.202	2.00	1.01	1160	0.381[b]	5.45	0.700	1186
0.159	2.26	0.702	1130	0.284[b]	5.67	0.501	1168
0.160	2.04	0.783	1110	0.186[b]	5.81	0.320	1135
0.150	2.42	0.620	1105				

[a] These experiments performed with $X_{CO}=0.0050$ ($X_{H_2}=0.0050$, $X_{O_2}=0.015$, $X_{Ar}=0.975$).

[b] These experiments performed with $X_{CO}=0.0050$ ($X_{H_2}=0.0050$, $X_{O_2}=0.0050$, $X_{Ar}=0.955$).

For all experiments the oscillogram of light intensity was analyzed by measuring vertical deflection as a function of time. The logarithms of the deflection readings were plotted versus time and a straight line was handdrawn through the data points. An experimental time constant α(seconds^{-1}) was calculated for each shock-tube run.

Two groups of experiments were performed: one with $[H_2]/[O_2]=0.33$ and one with $[H_2]/[O_2]=1.00$. In the first of these, three series of experiments were performed: one at high densities (5.5–9.2×10^{-2} mole/liter), one at medium densities (1.6–3.7×10^{-2} mole/liter), and one at low densities (0.15–1.4×10^{-2} mole/liter). In the second group, experiments were done in both a high-density (4.2–5.8×10^{-2} mole/liter) and a medium-density (1.1–2.5×10^{-2} mole/liter) range. The results of all the experiments are listed in Table I and plotted in Fig. 2. The function $\alpha/2[O_2]$ is plotted because in the limit of low density this function is independent of density, and at low densities and high $[H_2]/[O_2]$ ratios it is numerically equal to k_1.

CALCULATION OF RATE CONSTANTS

Values for k_1 and k_2, which are needed to calculate k_4, were obtained from the low-density data. These values for k_1 and k_2 were then used together with the medium and high-density data to calculate k_4. A different procedure was used for calculating each rate constant in order to obtain a self-consistent set of values which could account for all the experimental results.

Values for k_3 are needed in the calculations and were taken from the expression $k_3=6.15\times10^{10}\exp(-5.6$ kcal/RT) reported by Kaufmann and Del Greco.[11] Under our experimental conditions, the rate of Reaction (3) is much faster than that of any of the other reactions. This results in the calculated values for k_1, k_2, and k_4 being rather insensitive to the value used for k_3.

The procedures used to calculate k_1, k_2, and k_4 are as follows:

(1) Values for k_2 were obtained using a procedure similar to the one described in GS. The data used were from the lowest-density experiments of each group in order to minimize the importance of the value assumed for k_4. In this study, unlike the previous one, the difference in densities in the two sets of experiments had to be taken into account. A value for k_4 needed in this calculation was taken from the literature, and later, improved values were used as obtained below.

(2) Equation (I) was solved for k_1 for each of the low-density experiments mentioned in Item (1). In each calculation, the values for the variables used were (a) the experimentally determined α, (b) the concentrations behind the reflected shock wave assuming no reaction, (c) the k_2 value determined in Item (1), and (d) the same value for k_4 used in Item (1).

(3) Equation (I) was then solved for k_4. Values for k_1 and k_2 were taken from Items (1) and (2). A

[11] F. Kaufman and F. P. Del Greco, Symp. Combust. 9th Cornell Univ., Ithaca, N.Y., 1962, 659 (1963).
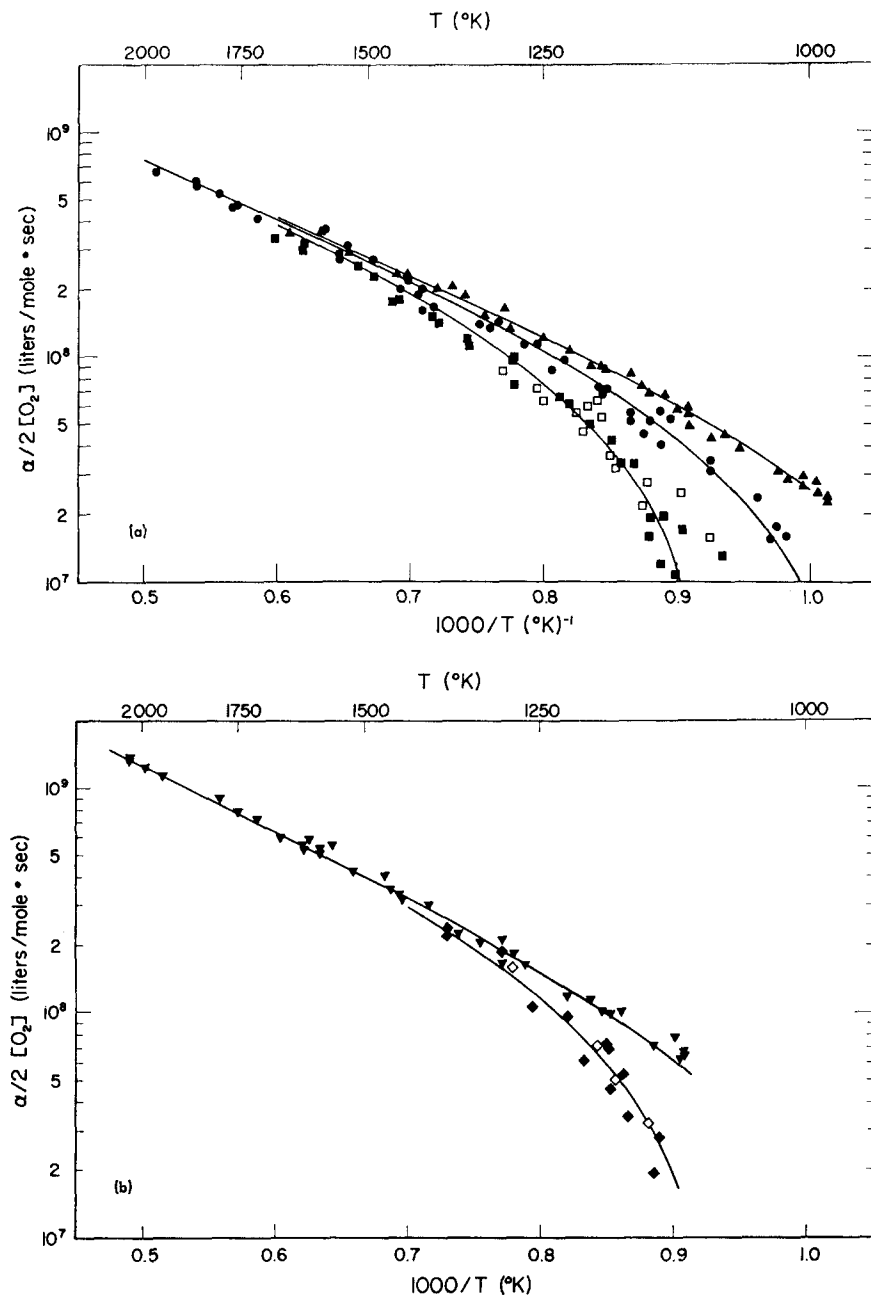
FIG. 2. Plots of $\alpha/2[O_2]$ derived from individual experiments (see Table I) plotted to reveal dependence on density and $[H_2]/[O_2]$ ratio. (Top) plot of experiments done with $[H_2]/[O_2]=0.33$. All mixtures 0.50% H_2-1.50% O_2. Symbols indicate density range and CO content. Remainder of mixture is argon. ▲, low density, 3.0% CO; ●, medium density, 3.0% CO; ■, high density, 3.0% CO; □, high density, 0.50% CO. (Bottom) plot of experiments done with $[H_2]/[O_2]=1.00$. All mixtures 0.50% H_2-0.50% O_2. Symbols indicate density range and CO content. Remainder of mixture is argon. ▼, medium density, 3.0% CO; filled-in diamond, high density, 3.0% CO; ◇, high density, 0.50% CO.

value for k_4 was obtained for each of the medium- and high-density experiments and a mean value was chosen as a "best value."

(4) Using this value for k_4, Items (1)–(3) were repeated until no further change occured in the calculated values of k_1, k_2, and k_4.

Using the final values for k_2 and k_4, a value for k_1 was calculated for every experiment performed. These k_1 values cover the temperature range 975°–2060°K (see Fig. 3). Fitting k_1 to an Arrhenius expression yields $k_1=9.54\times10^{10} \exp(-14.7 \text{ kcal}/RT)$.

Our experiments were conducted under conditions which are not favorable for obtaining an accurate indication of the magnitude of k_2. The k_2 values calculated in Item (1) scattered sufficiently so that no meaningful activation energy could be assigned to our values. Therefore, an average value for k_2 was chosen at 1500°K and an Arrhenius expression was generated by assuming an activation energy of 10.2 kcal/mole. This activation energy is exactly the same as that reported in two recent studies[12,13] and is close to that

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[12] A. A. Westenberg and N. de Haas, J. Chem. Phys. **46**, 490 (1967).
[13] E. L. Wong and A. E. Potter, J. Chem. Phys. **43**, 3371 (1965).

given in several others. The value chosen for k_2 at $1500°K$ is $1.98×10^9$, which yields the Arrhenius expression $k_2=5.6×10^{10} \exp(-10.2 \text{ kcal}/RT)$.

The calculated values for k_4 depend strongly on the value assumed for k_1 and only to a minor extent on the values used for k_2 and k_3. This is because Reaction (1) is the slow step in the branching mechanism under our experimental conditions and is almost rate limiting. Using the values for k_1 and k_2 obtained in this study, values for k_4 were calculated for the medium- and high-density experiments.

The error limits for the k_4 values vary from $±30\%$ at the low-temperature end to over $±100\%$ at the high-temperature end of this study. This change in accuracy is a result of the decreasing effect of Reaction (4) in the branching kinetics as the temperature increases and the density decreases. These error limits were obtained by assigning a $±20\%$ over-all uncertainty to $\alpha/2[O_2]$. The calculated values of k_4 with error limits less than $±50\%$ are shown in Fig. 4. From these values we have chosen the mean value $k_4^{Ar}=3.3×10^9$ at $1100°K$ as our best value and assign it an accuracy of $±30\%$.

DISCUSSION

Kinetic considerations due to the presence of CO in the H_2-O_2 system were discussed in GS. In this study an additional consideration is important because results were obtained from high-density experiments. The reaction

$$O+CO+M \xrightarrow{k_5} CO_2+M \qquad (5)$$
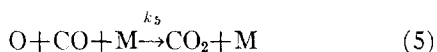
is an alternate recombination path to Reaction (4) and if ignored could possibly result in a high value being calculated for k_4. The effect of Reaction (5) was tested both theoretically and experimentally. Reaction (5) was added to the kinetic mechanism and a new
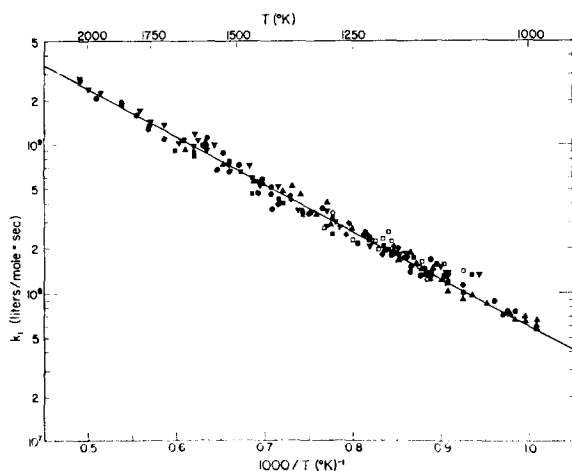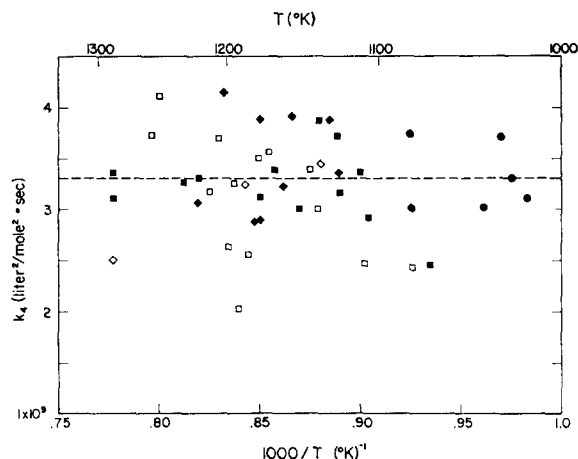
FIG. 4. Plot of all k_4^{Ar} values with experimental error limits less than $±50\%$. Error limits vary from $±30\%$ on the low-temperature end to $±50\%$ on the high-temperature end. Line through points is the mean value $k_4^{Ar}=3.3×10^9$ liter^{2}mole^{-2}·sec^{-1}. Symbols are the same as in Fig. 2.

cubic equation was obtained for α which in turn was solved for k_4^{Ar}. Using a value $k_5^{Ar}=1×10^8$, which was recently reported[14] as an "upper limit" to k_5^{Ar}, the new k_4^{Ar} values were reduced by less than 10%. Several experiments were performed with a lower CO content (0.5% vs 3.0%) and k_4 values were calculated ignoring Reaction (5) (open symbols in Fig. 4). Within our experimental scatter no difference between these values and the ones with 3% CO was discernable. Thus, we consider Reaction (5) to be of negligible importance in this study.

Another recombination reaction,

$$H+CO+M \xrightarrow{k_6} HCO+M, \qquad (6)$$
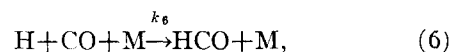
could not be quantitatively taken into account as no values for k_6 have been reported. Preliminary results reported by Thrush[15] indicate k_6 is much slower than k_4. Again if Reaction (6) were important, the values calculated for k_4^{Ar} from experiments performed with different CO concentrations should have been noticeably different.

The curves drawn through the experimental points in Fig. 1 were generated by solving Eq. (I) for $\alpha/2[O_2]$ using (a) the values for k_1, k_2, and k_4 obtained in this study, (b) the k_3 values of Kaufmann and DelGreco, and (c) a smoothed density function $[M]=M(T)$ obtained from the experimental densities (one for each line). The apparent scatter of the medium- and high-density points is due mainly to the difference in densities among the various experiments in the same density range. The $\alpha/2[O_2]$ variable is noticeably independent of density only in the low-density experiments done with the $[H_2]/[O_2]=0.33$ mixtures. The

FIG. 3. Plot of k_1 values obtained from each experiment in Table I. Line through points is $k_1=9.45×10^{10} \exp(-14.7 \text{ kcal}/RT)$ liter mole^{-1}·sec^{-1}. Symbols are the same as in Fig. 2.

[14] T. A. Brabbs and F. E. Belles, Symp. Combust. 11th Univ. Calif., Berkeley, Calif., 1966, 125 (1967).
[15] B. A. Thrush, Prog. Reaction Kinetics 3, 77 (1965).

experimental points along this curve give the best indication of the experimental scatter. When the density of each experiment is taken into account (as in the calculations of k_1), the "scatter" of the higher-density points decreases markedly.

COMPARISONS

k_1

The values for k_1 are essentially the same (15% higher) as in GS, and they were compared there with other literature values. There is now especially good agreement with the modified absolute rate theory expression for k_1 reported by Kurzius.[16] The larger temperature range for k_1 covered in this study makes it possible to narrow the error limits on the activation energy from ±1 to ±0.3 kcal. In GS, k_1 values were not calculated in the regime where Reaction (4) played a significant role because the possibility of further reactions of HO_2, the product of Reaction (4), could not be properly assessed. If further reactions were important, the values calculated for k_1 using Eq. (I) should depend markedly on the density and the $[H_2]/[O_2]$ ratio. The calculated k_1 values, obtained from experiments covering a 40-fold density range and a threefold $[H_2]/[O_2]$ range, all lie on the same line (see Fig. 4). We take this as sufficient evidence that the kinetic scheme [Reactions (1)–(4)] is adequate to describe the kinetics of the H_2–O_2 reaction during the induction period under our experimental conditions. Therefore we are able to determine k_1 even in the presence of a large effect from Reaction (4). The error limits on the magnitude of k_1 remain at ±20%, which included a 10% uncertainty in α and a possible additional 10% uncertainty arising from a systematic inaccuracy of ~2% in the reflected shock temperatures.

k_2

The k_2 expression $5.6 \times 10^{10} \exp(-10.2 \text{ kcal}/RT)$ which was derived from an assumed activation energy of 10.2 kcal and a mean value 1.98×10^9 at 1500°K, gives values about 30% higher than the earlier expression reported in GS. Due to the poor sensitivity of our experiments to the rate of Reaction (2), the error limits on our expression is ±40%, which included again a possible 10% uncertainty due to inaccuracies in the reflected shock temperature. The results of a recent study of Reaction (2) by Westenberg and de Haas[12] using a fast-flow reactor with ESR atom detection was not included in the comparison of k_2 values in GS. They report the expression $k_2 = 4.0 \pm 0.4 \times 10^{10} \times \exp(-10.2 \text{ kcal}/RT)$ which is valid from 300–1000°K. The k_2 values from this expression are 30% below ours and hence lie within our error limits.

Just as our experiments are not very sensitive to k_2, so the calculated values of $\alpha/2[O_2]$, k_1 and k_4 are not very sensitive to the value assumed for k_2. It was possible to fit our $\alpha/2[O_2]$ experimental points with the k_2 expression of Westenberg and de Haas which is possibly more accurate. However, a slightly better fit is obtained using our expression. So for internal self-consistency our expression was used.

k_4

Taking into account the slight negative activation energy for Reaction (4), our value for k_4^{Ar} of 3.3×10^9 at 1100°K is in very good agreement with the higher-temperature values reported by Getzinger and Blair[17] of 2.5×10^9 (1300°–1500°K) and the room-temperature values reported by Clyne and Thrush (8.0×10^9 at 293°K, 14.5×10^9 at 244°K, and 12.5×10^9 at 225°K).[18] Getzinger and Blair's value also results from a shock-tube study of the H_2–O_2 reaction. However, their investigation focused on the late stages of recombination in this reaction, and they employed a completely different analytic approach. Clyne and Thrush's values for k_4^{Ar} result from a study of the increased rate of H-atom removal in a flow system on the addition of molecular oxygen. Fitting these five values for k_4^{Ar} to an Arrhenius expression gives

$$k_4^{Ar} = (2.00 \pm 0.25) \times 10^9 \exp[(870 \pm 70 \text{kcal})/RT]$$

(II)

and to an expression of the form $k_4^{Ar} = A/T^n$ yields

$$k_4^{Ar} = (1.5 \pm 0.7) \times 10^{12} T^{-0.88 \pm 0.08}. \quad \text{(III)}$$

One other value for k_4^{Ar}, 8.25×10^9 at 1000°K, has been reported by Skinner and Ringrose.[19] Ignition delays in H_2–O_2–Ar gas mixture were measured at low temperatures and high densities where Reaction (4) is important. These delays were accounted for by varying rate constants in an ignition mechanism which included Reactions (1)–(4), and intiation reaction

$$H_2 + O_2 \xrightarrow{k_0} 2OH,$$

the reaction

$$HO_2 + H_2 \xrightarrow{k_{11}} H_2O_2 + H,$$
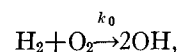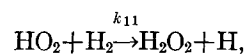
and several other recombination reactions. Their higher value for k_4 resulted in part for the high value they assigned to k_{11}. Since Reaction (11) essentially

[16] S. C. Kurzius, Symp. Combust. 10th Univ. Cambridge, Cambridge, England, 1964, 385 (1965).

[17] R. W. Getzinger and L. S. Blair, Paper presented at the Sixth International Shock Tube Symposium, Freiburg, Germany, April 1967. R. W. Getzinger and G. L. Schott, J. Chem. Phys. **43**, 3237 (1965), reported an earlier value for $k_4^{Ar} = 1.42 \times 10^9$ using virtually the same experimental procedure as is reported in the Freiburg paper.
[18] M. A. A. Clyne and B. A. Thrush, Proc. Roy. Soc. (London) **A275**, 559 (1963).
[19] G. B. Skinner and G. H. Ringrose, J. Chem. Phys. **42**, 2190 (1965).

destroys the effect of Reaction (4), a high k_4 is needed to account for the long ignition delays. Their k_{11} is 10^3 times higher than that reported by Voevodsky.[20] In our study, if k_{11} has the value reported by Skinner and Ringrose, we would have obtained markedly different k_4 values in experiments done at different $[H_2]/[O_2]$ ratios. Since we did not observe this we conclude that k_{11} is much smaller than the value reported by Skinner and Ringrose and that their k_4^{Ar} is consequently too high.

Several high-temperature values for k_4 have been reported for other third bodies. The only one reported above $1000°K$ is a value for $k_4^{H_2O}$ of 100×10^9 derived by Fenimore and Jones from flame studies near $1350°K$.[21] Agreement with our results can be achieved by using the relative efficiency $k_4^{H_2O}/k_4^{Ar} \approx 30$, which is the value for this ratio reported by Getzinger and Schott[22] and close to the value of 18 recently determined by Getzinger and Blair for this temperature range.[17] The apparent agreement might well be fortuitous, since the error limits on Fenimore and Jones' results are rather large and the relative efficiency of H_2O as a third body is still somewhat uncertain. Values for $k_4^{H_2}$ have been obtained near $800°K$ from second explosion limit studies of the H_2-O_2 reaction. These studies[23] are in close agreement with one another and report values for $k_4^{H_2}$ near 8×10^9. Converting this to a value for k_4^{Ar} gives 1.4×10^9 (assuming the presently accepted ratio $k_4^{H_2}/k_4^{Ar} \approx 5$). This value is a factor of 3 below a value for k_4^{Ar} at $800°K$ obtained using Eq. (II). Considering that two corrections have to be made—one for relative efficiencies and one for temperature—dis-

agreement is not serious but is definitely outside the error limits of the studies involved. No explanation is offered at this time to account for this discrepancy.

CONCLUSIONS

The end-on technique provides an accurate means of making measurements during the induction period of chain-branching reactions. Since during this period radical concentrations are low, only those reactions which have a single radical reactant have an appreciable rate. Hence, this technique allows one to study combustion processes unperturbed by radical–radical reactions. In the case of the H_2-O_2 reaction, use of the end-on technique has resulted in the determination of values for k_1, k_2, and k_4.

Only those recombination reactions involving one radical reactant are important during the induction period, and therefore the end-on technique provides a useful and sensitive method for studying these reactions. Since this technique provides a method of determining *both* the chain-branching rate constants and the recombination rate constant, the only information which must be assumed is the mechanism of the reaction during the induction period (excluding the initiation reaction). Such mechanisms will be relatively elementary since they exclude radical–radical reactions and they can be rigorously tested using data from experiments performed under a wide range of initial conditions.

ACKNOWLEDGMENT

[20] V. V. Voevodsky, Symp. Combust. 7th London, England, 1958, 34 (1959).

[21] C. P. Fenimore and G. W. Jones, Symp. Combust. 10th Univ. Cambridge, Cambridge, England, 1964, 489 (1965).

[22] See R. W. Getzinger and G. L. Schott in Ref. 17.

[23] For a review of these studies see Ref. 15, p. 78 and Ref. 18, p. 571.

[24] J. W. Linnett and N. J. Selley, Z. Physik. Chem. (Frankfurt) 37, 402 (1963).