SHOCK TUBE STUDY OF THE $H+O_2+Ar \rightarrow HO_2+Ar$ REACTION USING A NEW END-ON TECHNIQUE

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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 constant of this reaction for M=Ar (k_4^{Ar}) in the temperature range 1125-1370°K. The purpose of this study was twofold: first, to obtain accurate values of this constant for use in the analysis of future shock tube studies of combustion reactions (which are most often studied in a high argon dilution) 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 and known rate constants.

The significant reactions during the induction period of the H_2-O_2 reaction are:[1]

$$H_2 + O_2 \xrightarrow{R_0} O, H, OH \qquad (0)$$

$$H + O_2 \xrightarrow{k_1} OH + O \qquad (1)$$

$$O + H_2 \xrightarrow{k_2} OH + H \qquad (2)$$

$$OH + H_2 \xrightarrow{k_3} H_2O + H \qquad (3)$$

$$H + O_2 + M \xrightarrow{k_4} HO_2 + M \qquad (4)$$

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. $[O] = [O]_o e^{\alpha t}$] at essentially constant temperature and pressure. Kondratiev[1] and others have shown that this exponential growth constant α is the positive root of the equation

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

where $K_1 = k_1[O_2]$, $K_2 = k_2[H_2]$, $K_3 = k_3[H_2]$ and $K_4 = k_4[O_2]$. Using literature values for k_1-k_3 and the experimentally determined values for α and [M], Equation (I) was solved for k_4.

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 $O + CO \rightarrow CO_2 + h\nu$ was monitored. Since the emission intensity is proportional to [CO][O] and since the concentration of CO is constant during the induction period, the emission will exhibit the same exponential growth as the O-atoms. To obtain sufficient emission intensity for our induction period measurements, we used a special end-on technique, in which we studied the reaction behind the reflected shock wave by monitoring the total light emitted axially through a 7.6 cm diameter window mounted in the end flange of the shock tube. Under suitable conditions, the exponential growth constant of the integrated emission observed by this technique is identical to that for the free radical growth during the induction period.

The apparatus and experimental techniques were basically the same as those described earlier and therefore will only be summarized here.[2] The 10 cm diameter stainless steel shock tube used in this study has a 3.96 meter long test section and a 1.82 meter long driver section. Five thin film heat guages used to measure the shock velocity are mounted 25.4 cm apart along the tube, the last one located 15.0 cm from the end of the shock tube. The end flange of the shock tube was fitted with a 10 cm diameter and 1.25 cm thick Pyrex glass disk, masked on the outside to provide a 7.6 cm diameter axial window. A plano-convex lens (focal length 57.1 cm, diam. 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 am Amperex 150 AVP photomultiplier tube (S-11 response) located behind the aperture. The output of the cathode follower was directed to a Tektronix 545 oscilloscope (CA preamplifier) fitted with a Polaroid camera. A thin film heat gauge deposited on the window provided the signal that triggered a single sweep of the oscilloscope upon arrival of the shock wave at the end of the tube.

All experiments were performed in gas mixtures containing 0.50% H_2 - 0.50% O_2 - 3.0% CO - 96% Ar with the exception of three runs made with the same H_2-O_2 amounts but with 0.50% CO and 98.5% Ar. The gases were taken from commerical cylinders and were purified by passing them through a Drierite-filled trap cooled to dry-ice temperature. Two sets of experiments were performed - a high density set with densities in the range of $4.2 - 5.8 \times 10^{-2}$ moles/liter and a low density set having densities between $1.1 - 2.5 \times 10^{-2}$ moles/liter.

DATA REDUCTION

The shock velocity at the end of the tube was obtained from extrapolation of the data from the five thin film gauges mounted near the end of the shock tube. Hugoniot calculations for conditions of no chemical reaction behind both incident and reflected shock waves were used to determine the temperature and concentration conditions in each experiment. In all experiments, the vertical deflection was read from the oscillogram and plotted as a function of time on semi-log paper. A straight line was hand drawn through the data points and an experimental time constant $\alpha(sec^{-1})$ was calculated for each. The results are listed in Table I.

Solving Equation I for k_4, we obtain

$$k_4 = \frac{-8\alpha'^3 - 4(k_1+k_2n+k_3n)\alpha'^2 - 2k_2k_3n^2\alpha' + 2k_1k_2k_3n^2}{4[M]\alpha'^2 + 2(k_2n[M] + k_3n[M])\alpha' + k_2k_3n^2[M]} \qquad \text{(II)}$$

where $\alpha' = \alpha/2[O_2]$ and $n = [H_2]/[O_2]$.

By using Equation II and the experimentally determined growth constants α, we obtained a value for k_4 for each high density experiment. These values are given in the last column of Table I and are plotted in Figure II.

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. To obtain accurate and self-consistent values for k_1 for our calculations, we solved Equation I for α and varied k_1 until the experimental α values at high temperature and low density (where Reaction 4 is unimportant) corresponded to the calculated value. The best fit was with an expression $k_1 = 1.25 \times 10^{11}\exp(-14.97\ \text{kcal/RT})$ which yields values 30% higher than the expression reported by Gutman and Schott.[2] The Arrhenius expressions for k_2 and k_3 used for both the α and k_4 calculations were $k_2 = 3.25 \times 10^{10}\exp(-10.0\ \text{kcal/RT})$ liter/mole-sec.[3] and $k_3 = 6.15 \times 10^{10}\exp(-5.90\ \text{kcal/RT})$ liter/mole-sec.[4] The lines drawn through the experimental points in Figure I are solutions to Equation I using: (1) the above values for k_1, k_2, and k_3; (2) a smoothed density function $[M] = M(T)$ obtained from the experimenatl densities (one for each line); and (3) the expression $k_4^{Ar} = 6.83 \times 10^{11}/T^{0.74}$ (liter^2/mole^2-sec) which is explained below. [Hereafter units of liter^2/mole^2-sec are implied for k_4.]

To obtain a temperature dependent function of k_4 for use in the above calculations and also for use in comparing our results with others at different temperatures, we evaluated the parameters in the expression $k_4^{Ar} = A/T^n$ by joining the point $k_4^{Ar} = 3.75 \times 10^9$ at 1087°K at the low temperature end of our study with a value of $k_4^{Ar} = 12.5 \times 10^9$ at 225°K reported by Clyne and Thrush.[5] The resulting expression is $k_4^{Ar} = 6.83 \times 10^{11}/T^{0.74}$.

The error limits for our k_4 values vary from ±30% at the low temperature end of our study to ±100% at the high temperature end. 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 limits were obtained from assigning a ±20% overall uncertainty to α' and are shown as error bars in Figure II.

Because of the rapidly increasing limits of error toward our higher temperature results, we have chosen the mean value $k_4^{Ar} = 3.75 \times 10^9$ liter^2/mole^2-sec at 1087° as our best value and assign it an accuracy of ±30%.

DISCUSSION

The effects of adding CO to the H_2-O_2 system were discussed previously.[2] However, in this study an additional consideration is important due to the high densities used here. The reaction $O + CO + M \xrightarrow{k_6} CO_2 + M$, although slow,

was taken into account. It was added to the kinetic mechanism and a new cubic equation was obtained for α, which in turn was solved for k_4^{Ar}. Using a value of 1×10^8 liter^2/mole^2-sec,[6], there was a negligible change in the calculated k_4. We performed four experiments with 0.5% CO and obtained from these experiments calculated k_4 values in agreement with the others performed with mixtures containing 3% CO.

Our results are virtually in complete agreement with the value for k_4^{Ar} recently reported by Getzinger and Blair.[7] They report a value of $k_4^{Ar} = 2.5 \times 10^9$ in the temperature range 1500-1700°K. Extrapolating our value to their temperature range, we calculate values 10-20% higher than theirs. Other values for k_4, especially for k_4^{H2}, have been reported near 800°K based on explosion-limit studies. These studies are in fair agreement with one another and report values for k_4^{H2} near 8×10^9 liter^2/mole-sec.[8] Converting these to a value for k_4^{Ar} gives 1.4×10^9 (assuming the presently accepted ratio $k_4^{H2}/k_4^{Ar} \cong 5$). At 800°K our k_4^{Ar} expression gives the value 6×10^9. No explanation is offered at this time to account for this large discrepancy. A value for $k_4^{H2O} = 100 \times 10^9$ has been reported by Fenimore and Jones from flame studies near 1350°K.[9] If this value is adjusted to give a value for k_4^{Ar} using $k_4^{H2O}/k_4^{Ar} = 20$, it yields a value somewhat higher but in good agreement with our k_4^{Ar} curve. The agreement might well be fortuitous, since their error limits are rather large and the correction for the relative efficiency of water is somewhat uncertain.

CONCLUSIONS

The end-on technique provides a 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 $H_2 + O_2$ reaction, use of the end-on technique has resulted in values for k_1, k_2, and k_4. In other systems where the mechanism is not clearly understood, measurements of the chain-branching coefficient under a variety of initial conditions could help to identify the important reactions.

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Table I

Experimental Results of induction period emission experiments

$X_{H_2} = 0.0050$; $X_{O_2} = 0.0050$; $X_{CO} = 0.030$; $X_{Ar} = 0.960$

Low Density Experiments

$\alpha \times 10^{-5}$ (sec^{-1})	[M] x 10^2 (mole/liter)	$\alpha' \times 10^8$ (liter/mole-sec)	T (°K)	$K_4^{Ar} \times 10^{-10}$ (liter^2/mole^2-sec)
1.44	1.096	13.300	2040	
1.48	1.096	13.500	2040	
1.40	1.152	12.130	2000	
1.38	1.206	11.140	1943	
1.15	1.298	8.860	1793	
9.8	1.274	7.700	1750	
1.01	1.382	7.310	1705	
0.728	1.238	5.890	1655	
0.836	1.528	5.490	1613	
0.920	1.466	5.280	1608	
0.921	1.584	5.820	1600	
0.808	1.510	5.350	1577	
0.783	1.510	5.180	1576	
0.813	1.498	5.430	1555	
0.705	1.650	4.270	1515	
0.702	1.740	4.040	1465	
0.562	1.614	3.480	1455	
0.602	1.840	3.300	1440	
0.511	1.608	3.180	1437	
0.527	1.744	3.020	1395	
0.434	1.856	2.220	1355	
0.418	2.024	2.060	1325	
0.391	1.880	2.080	1296	

Low Density Experiments

$\alpha \times 10^{-5}$ (sec^{-1})	$[M] \times 10^{2}$ (mole/liter)	$\alpha' \times 10^{8}$ (liter/mole-sec)	T (^{o}K)	$K_4^{Ar} \times 10^{-10}$ ($liter^2/mole^2$-sec)
0.339	2.040	1.660	1296	
0.359	2.020	1.780	1280	
0.333	2.080	1.600	1270	
0.250	2.138	1.170	1220	
0.240	2.080	1.150	1192	
0.206	2.070	1.000	1182	
0.218	2.200	0.990	1173	
0.202	2.000	1.010	1160	
0.159	2.260	0.702	1130	
0.160	2.040	0.783	1110	
0.150	2.420	0.620	1105	
0.160	2.410	0.673	1100	
0.142	2.120	0.670	1100	
0.150	2.536	0.592	1060	

High Density Experiments

1.035	4.75	2.180	1370	0.419
1.065	4.59	2.320	1370	0.337
0.885	4.75	1.865	1295	0.173
0.561	5.30	1.060	1260	0.458
0.522	5.44	0.960	1220	0.334
0.338	5.52	0.610	1200	0.453
0.404	5.56	0.727	1180	0.307
0.268	5.80	0.462	1175	0.511
0.383	5.54	0.690	1175	0.309
0.279	5.59	0.529	1160	0.404
0.198	5.77	0.343	1155	0.423
0.163	5.83	0.279	1125	0.362
0.113	5.92	0.191	1130	0.422
*0.832	5.22	1.590	1285	0.270
*0.381	5.42	0.700	1185	0.346
*0.284	5.67	0.501	1166	0.380
*0.186	5.81	0.320	1135	0.371

* Experiments performed with:
$X_{H_2} = 0.0050$; $X_{O_2} = 0.0050$; $X_{CO} = 0.005$; $X_{Ar} = 0.985$

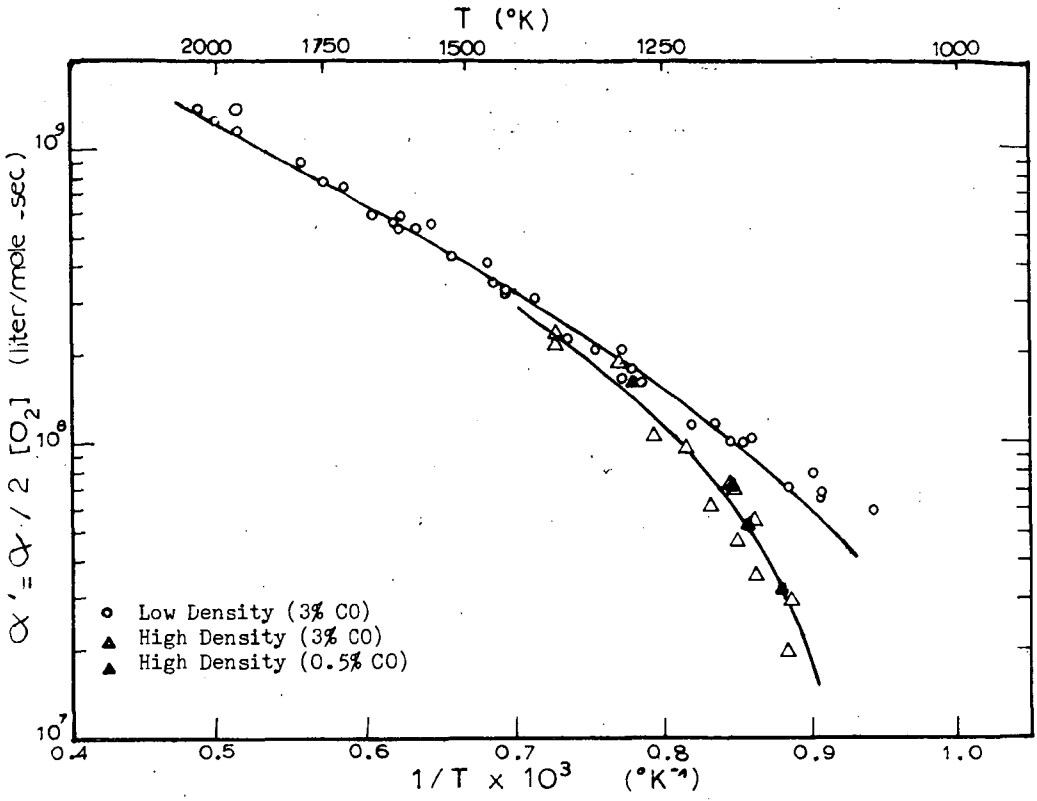

Figure I. Plot of $\alpha / 2 [O_2]$ vs. 1/T.

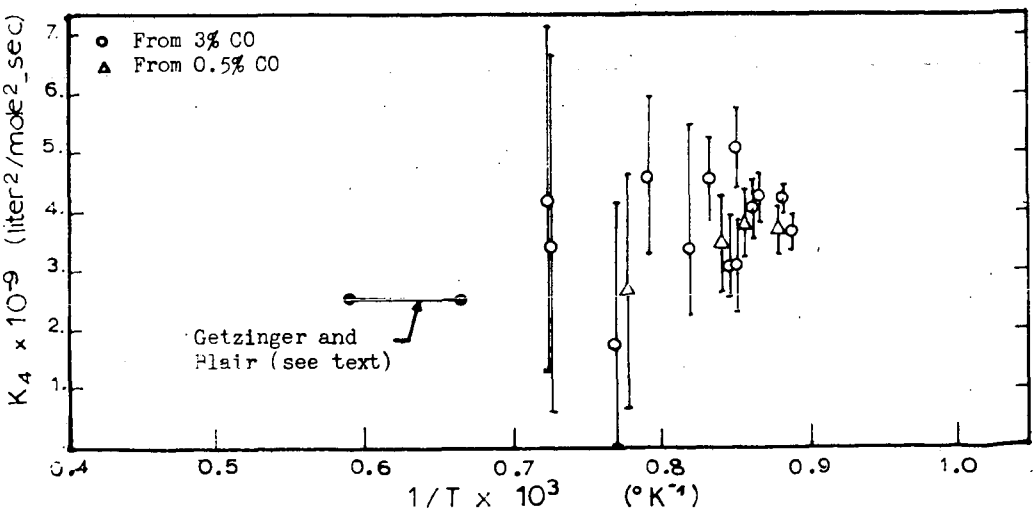

Figure II. Calculated values for k_4^{Ar} from corresponding points on high density curve in Figure I.