AnUJ# 33903

AD621199

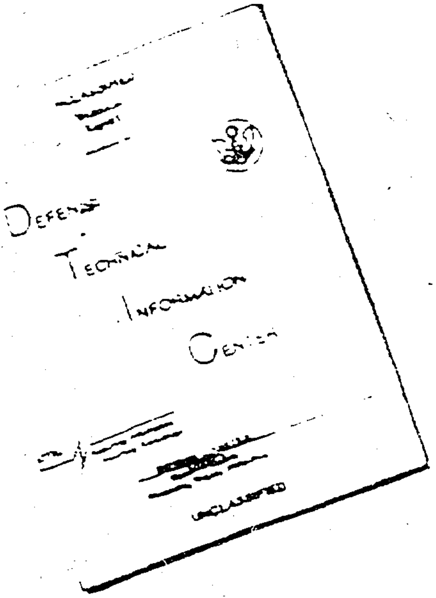
CLEARINGHOUSE
FOR [illegible] A. D
[illegible] MATION
[illegible] copy [illegible]
$ [illegible] 9.00

D [illegible]

A[illegible] 1965

T[illegible] E

Copies available
only to DDC users


DEFENSE
TECHNICAL
INFORMATION
CENTER
UNCLASSIFIED

um (International) on Combustion, pp. 295-302, The Combustion Institute, 1965

TUBE STUDY OF THE HYDROGEN–OXYGEN REACTION*

T. ASABA

Department of Chemistry, The University of Texas, Austin, Texas

W. C. GARDINER, JR.

Department of Chemistry, The University of Texas, Austin, Texas

AND

R. F. STUBBEMAN

Esso Research and Engineering Company, Linden, New Jersey

hydrogen–oxygen reaction was investigated using OH absorption and emission measnts of induction times over the temperature range of 1400°–2500°K. The dependence uction time on composition was studied to measure the relative influence of hydrogen xygen concentrations in determining the induction times. Comparison of experimental irements with computed values obtained from an analytic solution to the rate equawhich is presented in detail, showed that the results could be understood in terms of oefficient parameters which are in agreement with previous studies. The effect of slow ional relaxation of O_2 was investigated under conditions where the vibrational relaxation were comparable to the induction times. The results indicated that in normal studies lrogen–oxygen ignition kinetics no effect of slow vibrational relaxation will be observed.

Introduction

tudies of the hydrogen–oxygen reac- temperatures have been reported in . For the case of pressures low enough ecular reactions can be disregarded, bsence of wall effects, they have con- the dominant reactions of the induc- are:

$$H_2 + O_2 = 2\,OH \text{ (or H, O)} \qquad (0)$$

$$H + O_2 = O + OH \qquad (1)$$

$$O + H_2 = H + OH \qquad (2)$$

$$)H + H_2 = H + H_2O. \qquad (3)$$

all result of this branching-chain exponential growth of chain-carrier ons with little release of heat. Subower termolecular reactions lead to ical equilibrium and the release of issions of this set of reactions, with o additional experimental work, have shed.[1–6]

Theoretical Treatment

to investigate the agreement between tion of the induction period in terms of Reactions (0)–(3) and experimental results, a solution of the rate equations for these reactions is required under conditions appropriate to the experimental range of temperature, pressure, and composition. In an early paper using techniques similar to those employed here, Schott and Kinsey[1] employed partial steady-state approximations[5] and assumed constant hydrogen and oxygen concentrations in order to derive an expression for the rate of growth of hydroxyl-radical concentration. This led to a relation between oxygen concentration, induction time, and temperature, which could be compared with their experimental results. A different approach taken was numerical integration of the rate equations under the constraint of constant shock flow.[6,1]

The partial steady-state approximation used by Schott and Kinsey, and also in previous treatments of the induction period reactions for other kinds of experiments,[4] was based on the following considerations: Since Reaction (1) is 17 kcal endothermic, whereas Reactions (2) and (3) are about thermoneutral or exothermic ($\Delta E_2 = 3$ kcal, $\Delta E_3 = -16$ kcal), it was assumed that Reaction (1) was rate controlling and that the partial steady-state approximation could be applied to the concentrations of O and OH. Recent experimental work,[3,7] however, has shown that the rate coefficients of Reactions (1) and (2) are

---

erformed at The University of Texas.

actually about equal in the temperature range of interest here, and that the partial steady-state approximation cannot be applied to the concentration of O. This means that the analysis used by Schott and Kinsey is applicable only when the ratio of hydrogen to oxygen is very large.

We solved the system of rate equations for Reactions (0)-(3) without steady-state approximations or assumptions about the values of the rate coefficients. The rate equations are

$$d[\mathrm{OH}]/dt = [\mathrm{H}][\mathrm{O_2}]k_1 + [\mathrm{O}][\mathrm{H_2}]k_2 - [\mathrm{OH}][\mathrm{H_2}]k_3 + 2[\mathrm{H_2}][\mathrm{O_2}]k_0, \quad (4)$$

$$d[\mathrm{O}]/dt = [\mathrm{H}][\mathrm{O_2}]k_1 - [\mathrm{O}][\mathrm{H_2}]k_2, \quad (5)$$

$$d[\mathrm{H}]/dt = [\mathrm{O}][\mathrm{H_2}]k_2 + [\mathrm{OH}][\mathrm{H_2}]k_3 - [\mathrm{H}][\mathrm{O_2}]k_1. \quad (6)$$

During all but the very last part of the induction period, when Reactions (0)-(3) no longer suffice to describe the reaction system, the concentrations of hydrogen and oxygen remain constant. Equations (4)-(6) then can be written

$$dx/dt = za + yb - xc + 2R_0, \quad (7)$$

$$dy/dt = za - by, \quad (8)$$

$$dz/dt = yb + xc - za, \quad (9)$$

where $x = [\mathrm{OH}]$, $y = [\mathrm{O}]$, $z = [\mathrm{H}]$, and a, b, c and R_0 are constants at a given temperature and starting composition. The initial conditions are $x = y = z = 0$. The solution is

$$x = \text{coef } A \exp(B_A \cdot t) + \text{coef } B \exp(B_B \cdot t) + \text{coef } C \exp(B_C \cdot t),$$

where

$$B_A = \tfrac{1}{3}[-(a+b+c)] + \tfrac{2}{3}[-3bc + (a+b+c)^2]^{1/2} \cos \tfrac{1}{3}\phi$$

$$B_B = \tfrac{1}{3}[-(a+b+c)] + \tfrac{2}{3}[-3bc + (a+b+c)^2]^{1/2} \cos \tfrac{1}{3}(\phi + 2\pi)$$

$$B_C = \tfrac{1}{3}[-(a+b+c)] + \tfrac{2}{3}[-3bc + (a+b+c)^2]^{1/2} \cos \tfrac{1}{3}(\phi + 4\pi)$$

$$\phi = \cos^{-1} \frac{2(a+b+c)^3 - 9(a+b+c)bc - 54\,abc}{2\{-[3bc - (a+b+c)^2]^3\}^{1/2}}.$$

$$\begin{bmatrix} \text{coef } A \\ \text{coef } B \\ \text{coef } C \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 \\ \dfrac{B_A + c}{2b + B_A} & \dfrac{B_B + c}{2b + B_B} & \dfrac{B_C + c}{2b + B_C} \\ \dfrac{(B_A + b)(B_A + c)}{a(2b + B_A)} & \dfrac{(B_B + b)(B_B + c)}{a(2b + B_B)} & \dfrac{(B_C + b)(B_C + c)}{a(2b + B_C)} \end{bmatrix}^{-1} \begin{bmatrix} 0 \\ R_0/b \\ R_0/a \end{bmatrix}$$

The constants appearing in the solution can be computed readily for any given temperatures, compositions, and rate coefficients.[14]

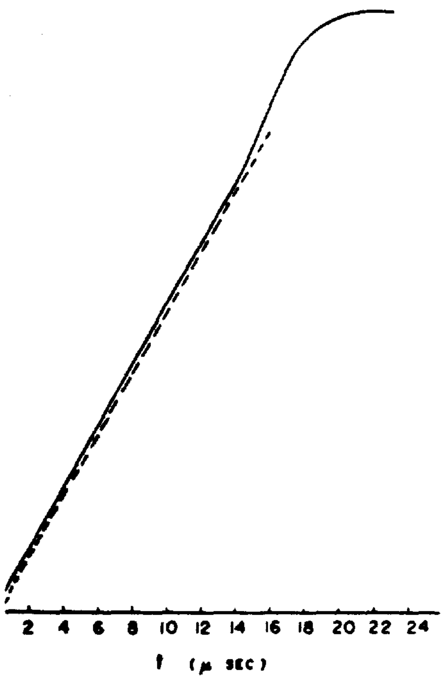
This solution incorporates assumptions of constant temperature and reactant concentration, ignores the fact that the experiments are actually performed in flowing gas, and allows chain initiation only by formation of OH. The last assumption is, in fact, not necessary; the solution is only slightly complicated by allowing H and O to be produced in initiation steps. There appears to be no gain in doing this at present, however, since little is known about the homogeneous reactions producing chain centers, and the interpretation of our results would be unaffected thereby. There is, likewise, little prospect that eliminating the other assumptions by analytical means, if it is possible at all, would be of advantage for present purposes. This can be shown by comparing the rate of increase of OH concentration in a shock-tube experiment, as computed using the analytic solution with a straightforward numerical integration of the rate equations without simplifications given by Schott and Kinsey. Figure 1 shows that the two solutions give identical results until well after the observed end of the induction period.

Similar treatments of the induction period kinetics have been presented by other authors.[4,8,9] They have shown that there are several kinds of simplifications which can be made in the equations. Two of the three roots are negative, and can be shown by direct calculation to give no contribution, even as transients, to the physically significant growth of radical concentrations. One has only to consider, therefore, the single positive root. The constants appearing in the equations can then be examined for size under a given set of experimental conditions, and superfluous ones omitted from the computation. One can then search for algebraic simplifications, and obtain expressions which can be plotted for comparison with experimental data, and inspected for insight into the chemical kinetics.

We have chosen an alternative procedure. For presentation of experimental data, a graph of

· t_i versus inverse temperature was y Schott and Kinsey to be useful. It will ater that such a plot has little theoretical nce, but it serves well for inspection of nt between predictions and experiments, l allow the present experiments to be d with the results of Schott and Kinsey. e, our computational procedure was l to develop theoretical relationships log $[O_2] \cdot t_i$ and $1/T$ for various experi- mixtures and various sets of trial rate- at expressions. The complete solution grammed for a digital computer, and f t_i were computed as the time between ating and attainment of OH concentra- ar 10^{-6} moles per liter, which is assumed e detection threshold of our apparatus.[18] an then determine the dependence of the n-period reactions on concentration of n and oxygen in the following way. The ng rate can be written formally as

$$d(\log x)/dt = k[O_2]^m[H_2]^n.$$



1. Comparison of analytic solution with al integration of rate equations. Rate coeffi- nd experimental conditions identical with Fig. 2, Ref. 1. – – –, analytical solution; merical integration.

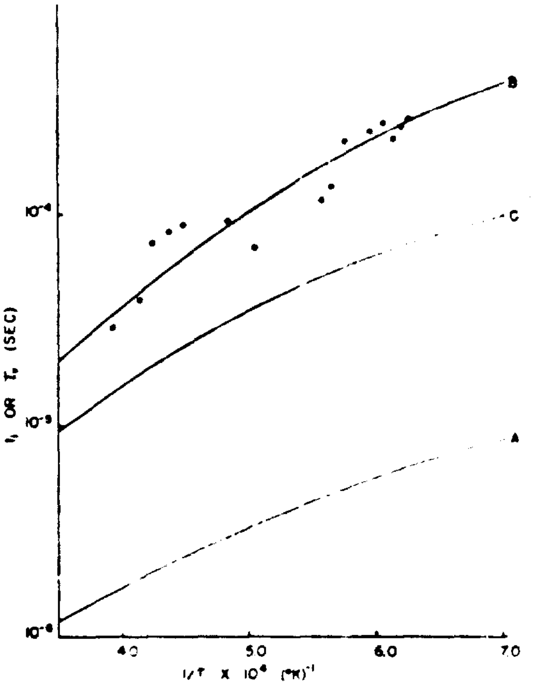


FIG. 2. Comparison of experimental induction times with calculated vibrational relaxation times for oxygen. Solid circles are measured induction times for $Ar:H_2:O_2 = 98:1:1$. Curve A, vibrational relaxation time for $He:Kr:D_2:O_2 = 68:30:1:1$. Curve B, vibrational relaxation time for $Kr:D_2:O_2 = 98:1:1$. Curve C, vibrational relaxation time for $Ar:D_2:O_2 = 98:1:1$. Starting pressure in each case, 10 Torr.

Integrated from shock heating to the observed end of the induction period, assumed to be a certain chain-center concentration, this yields

$$k[O_2]^m[H_2]^n \cdot t_i = \text{constant}.$$

or, in logarithmic form,

$$\log(\text{constant}) = \log k + m \log[O_2] + n \log[H_2] + \log t_i.$$

For one concentration held constant, the slope of log $1/t_i$ versus log [ ] for the other concentration gives m or n. In this way, the effective molecularity of the induction-period reactions can be determined from the experimental values for the rate constants for Reactions (0)–(3).

Vibrational Relaxation Effects

At the upper end of the temperature range studied in our experiments, the induction periods begin to be so short that they approach the vibrational relaxation time of oxygen. The question then arises as to whether the rates of Reactions (0) or (1) may be affected by the finite rate of equilibration of the first and second vibrational levels of oxygen, which are populated, at 2000°K, with 22% and 7%, respectively, of the total oxygen. Recently, accurate experimental data have become available on the efficiency of various collision partners for vibrational equilibration of oxygen.[10] A study was made to determine if there would be a possibility of observing the induction periods of the hydrogen–oxygen reaction at various degrees of vibrational equilibration of oxygen.

For the usual composition range employed in this and other shock-tube studies of the hydrogen-oxygen reaction, the greatest contribution to the oxygen relaxation comes from collisions with hydrogen, even when hydrogen is present in concentrations lower than 1%. This concentration is about the lower limit for accurate measurements of induction times in our apparatus. Calculation showed that it would not be possible to obtain any conditions where the induction time would be both shorter than the vibration relaxation time and still measurable with 1% hydrogen in the experimental mixture. A different situation is obtained when deuterium is substituted for hydrogen. The large increase in reduced mass for deuterium oxygen collisions slows down the calculated vibrational relaxation times to the point where they do indeed become as long as induction times, under conditions accessible to study in our apparatus. Additional lengthening of the relaxation times is obtained by using krypton rather than argon as the diluent gas. In Fig. 2, the calculated vibrational relaxation times for two deuterium oxygen mixtures, one diluted with krypton and one diluted with krypton and helium, are compared with induction times for 10 Torr starting pressure. It was necessary to add krypton to the helium in order to obtain sufficiently high temperatures with our apparatus. The induction times in Fig. 8 are our results for an experimental mixture containing 1% hydrogen, 1% oxygen, and 98% argon. Relaxation times for krypton were obtained by extrapolation of experimental data for helium and argon. Relaxation times for deuterium were assumed to be the same as for helium, according to the suggestion by White.[13]

Experimental

The data presented here are induction periods in hydrogen–oxygen argon mixtures heated to reaction temperatures in the range 1400°–2400°K by incident shock waves. Starting pressures ranged from 5 to 15 Torr, with most of the experiments at 10 Torr. The induction period was experimentally defined as the time between shock heating and first observable trace of hydroxyl-radical concentration, multiplied by the density ratio in the shock to convert from observer to gas time.

Our apparatus is of conventional design (Fig. 3). The shock tube was constructed of 1.75 in. × 4 in. aluminum tubing. A series of flush, de-

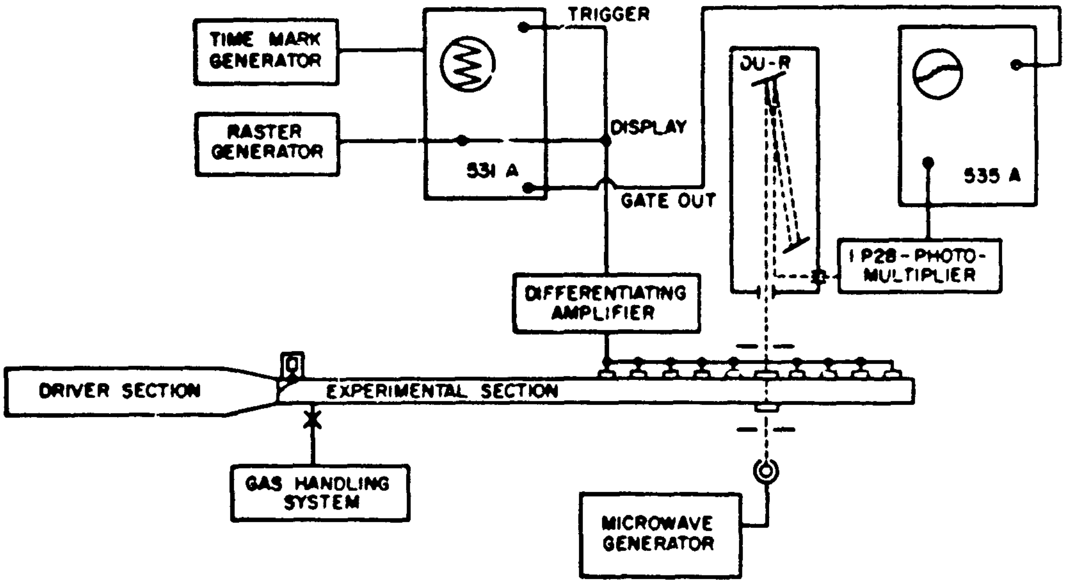
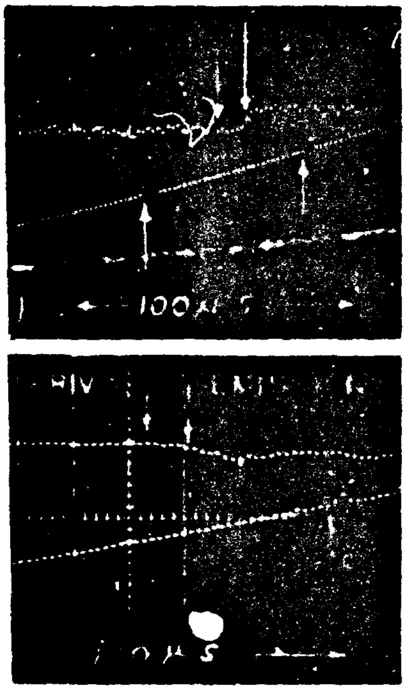


FIG. 3. Block diagram of apparatus.



Upper photograph: Absorption of 3067 ; OH. The diagonal trace records signals ance gauges. Experimental conditions :O_2 = 98:1:1; starting pressure, 10 Torr; perature, 2350°K. Lower photograph: om OD, triangular 30A bandpass cen-080 Å. Experimental conditions were = 98:1:1; starting pressure, 10 Torr; erature, 2480°K.

tinum resistance gauges, spaced on of the observation station, provided velocity measurements. The amplified e displayed together with time marks sweep oscilloscope. Shock velocities were computed by graphical analysis of the raster sweep photographs. Arrival of the shock wave at the observation point could be measured to about ±1 microsecond. The observation station was a pair of flush quartz windows on opposite sides of the shock tube.

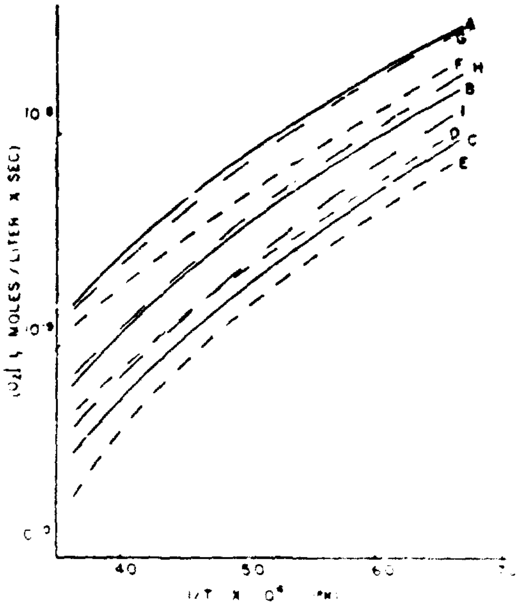


FIG. 5. Sensitivity of computed lines to variation of input-rate coefficients and cutoff concentration. Data for each line from Table II.

The lamp for absorption measurements consisted of a microwave discharge (2.45 gc, 100 W) in about 10 Torr argon containing a trace of bismuth vapor.[11] The bismuth resonance line at 3067 Å, which coincides with the $R_2 1 0$ line of the 0-0 transition of the $^2\Sigma$–$^2\Pi$ system of OH, was isolated after collimation by slits with a Beckman DU monochromator, and the intensity measured

TABLE I

Composition of experimental mixtures

Hydrogen	Oxygen	Deuterium	Argon	Krypton	Helium	Ratio
0.032	0.010	0	0.958	0	0	3.2
0.020	0.010	0	0.970	0	0	2.0
0.010	0.010	0	0.980	0	0	1.0
0.0029	0.010	0	0.987	0	0	0.29
0.0017	0.010	0	0.988	0	0	0.17
0	0.010	0.010	0	0.98	0	1.0
0	0.010	0.010	0	0.30	0.68	1.0
0.010	0.030	0	0.960	0	0	0.33

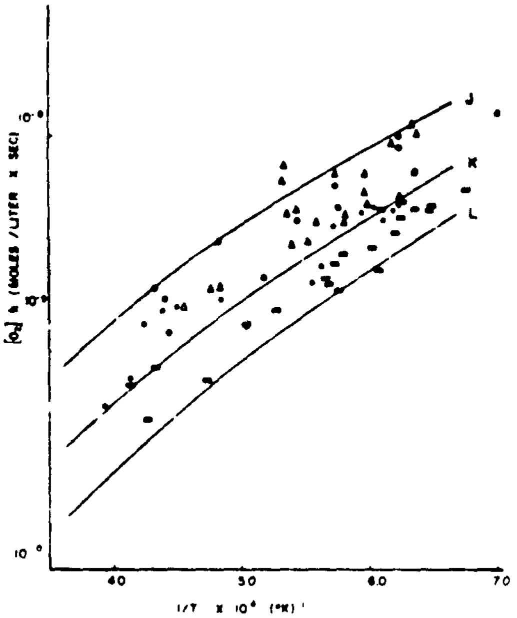


Fig. 6. Induction times for OH absorption. Solid triangles, $H_2:O_2 = 0.17:1$; open triangles, $H_2:O_2 = 0.29:1$; open circles, $H_2:O_2 = 1:1$; open rectangles, $H_2:O_2 = 2:1$; solid rectangles, $H_2:O_2 = 3:1$; solid circles, $H_2:O_2 = 1:3$.

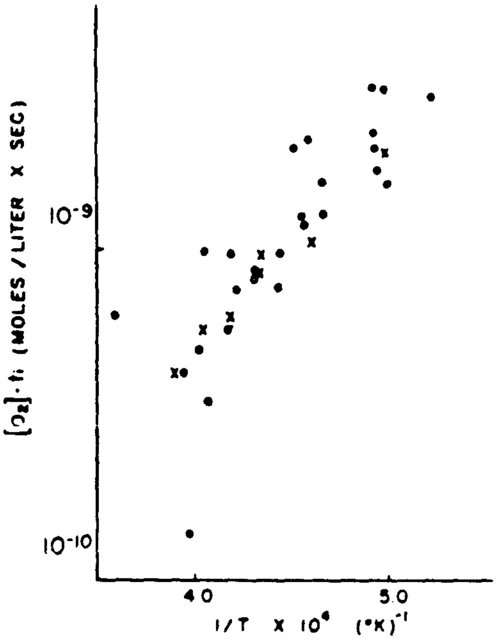


Fig. 7. Induction periods to onset of $^2\Sigma$–$^2\Pi$ (0–0) emission in vibrational relaxation experiments. Crosses, $Ar:H_2:O_2 = 98:1:1$; open circles, $He:Kr:H_2:O_2 = 68:30:1:1$; solid circles, $Kr:D_2:O_2 = 98:1:1$.

with a 1P28 photomultiplier. The anode signal was applied to the grid of a cathode follower, the output was adjusted for about 2 μsec response time, and displayed as a single sweep on a Tektronix 535A oscilloscope. For measurement of short induction periods, the output of the photomultiplier was displayed on an oscilloscope with a trace chopped at a crystal-controlled frequency of 1 mc, to allow simultaneous recording of velocity markers and absorption or emission on one photograph. A sample oscillogram is shown in Fig. 4.

Gas mixtures were prepared manometrically in a conventional vacuum system. Commercial cylinder gases were used without purification.

TABLE II

Input data for computations

Line	$[H_2]/[O_2]$	Cutoff	$\log A_0$	E_0	$\log A_1$	E_1	$\log A_2$	E_2	$\log A_3$	E_3
A	0.33	10^{-8}	11.0	70,000	11.86	16,900	9.4	7700	10.8	5900
B	1.0	10^{-8}	11.0	70,000	11.86	16,900	9.4	7700	10.8	5900
C	3.0	10^{-8}	11.0	70,000	11.86	16,900	9.4	7700	10.8	5900
D	1.0	10^{-8}	11.0	70,000	11.86	16,900	9.9	7700	10.8	5900
E	1.0	10^{-9}	11.0	60,000	11.86	16,900	9.9	7700	10.8	5900
F	1.0	10^{-9}	10.0	70,000	11.36	16,900	9.9	7700	10.8	5900
G	0.33	10^{-9}	11.0	70,000	11.36	16,900	9.9	7700	10.8	5900
H	1.0	10^{-9}	11.0	70,000	11.36	16,900	9.9	7700	10.8	5900
I	3.0	10^{-9}	11.0	70,000	11.36	16,900	9.0	7700	10.8	5900
J	0.33	0.3×10^{-9}	11.0	70,000	12.0	16,900	10.0	7700	10.8	5900
K	1.0	0.3×10^{-9}	11.0	70,000	12.0	16,900	10.0	7700	10.8	5900
L	3.0	0.3×10^{-9}	11.0	70,000	12.0	16,900	10.0	7700	10.8	5900

lists the compositions of the mixture

Results

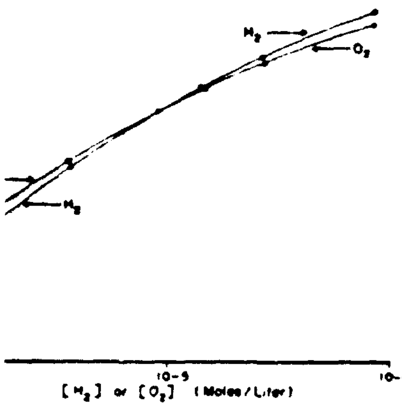
nsitivity of theoretical lines for the $[O_2] \cdot t_i$ vs inverse temperature to n input rate constants and OH appear- entration, is shown in Fig. 5. Starting input rate constants were taken from y article of Kaufman and Del Greco[3] suggestions of Baldwin[12] and Clyne.[7] erimentally measured induction periods hydrogen–oxygen mixtures are shown The calculated lines correspond to the the rate constants given in Table II.

on periods in deuterium–oxygen mix- e measured to onset of OD emission at n Fig. 7, the results for the two different ital mixtures are shown, together with ents of the induction period determined nission at 3070 Å for a $H_2 + O_2 + 98$ re.

tion of the quantities m and n is illus- Fig. 8.

Discussion

sults presented in Fig. 6 demonstrate ction times in the hydrogen–oxygen n shock waves depend on the concentrations of both hydrogen and oxygen. They indicate also that the degree of dependence on composition and temperature can be predicted in reasonable agreement with experiment using rate-coefficient expressions for the elementary reactions involved that are in accord with previous experimental studies.



Investigation of effective molecularity of period reactions. Slope of H_2 curve yields ty for H_2, slope of O_2 curve yields molec- O_2. Temperature, 1800°K. Starting pres- orr for 98:1:1 mixture, and adjusted to reactant concentration constant for other

It is significant that, for reasonable values of appearance concentration and rate coefficients, the assumed induction period scheme allows the calculation of induction periods which reproduce both the temperature and concentration dependence of the reaction. Upon examination of the sensitivity of the solution to variation of the rate-coefficient parameters and appearance concentration, it is found that the slope, position, curvature, and composition dependence of the plotted $\log [O_2] \cdot t_i$ values depend strongly on the set of rate-coefficient parameters, except that k_3, being substantially greater than k_2 under all conditions, has little effect on the predicted curves. Too high a value for k_0 has the end effect of curving the plotted induction periods more strongly downward at high temperatures, since this causes the linear portion of the OH-concentration increase to continue to higher OH concentrations. The activation energy given to k_1 affects the slope of the calculated lines, while that given to k_2 affects only the position of the lines. This is a consequence of the fact that the activation energy of k_1 is considerably larger than the activation energy of k_2. It would be possible to reproduce the data of our experiments with other than the rate coefficient parameters indicated in Table II; one then loses, however, the correct extrapolations to data obtained in experiments at lower temperatures.

In the experiments performed to test for vibrational relaxation effects, a clear lengthening of the induction period for the vibrationally cold mixture can be seen. The scatter in the results for the vibrationally cold mixture appears to be greater than for other mixtures. This may be an effect of driver-gas mixing due to nonideal diaphragm rupture, as has been noted in other sensitive shock-tube experiments. It is clear from the magnitude of the induction period lengthening that no effect of vibrational relaxation will be observed in mixtures containing hydrogen and argon.

The effective molecularity of the induction period reactions depends on the composition of the reacting mixture and the temperature. Values of m and n under typical conditions of temperature (1800°) and composition are found to be $0.4 < m < 0.6$, $0.5 < n < 0.8$. The dependence upon oxygen concentration, for the temperature range of these experiments, is less than the dependence upon hydrogen concentration for equivalence ratios within a factor of 5 from stoichiometric. At lower temperatures, the reverse situation prevails, due to the higher activation energy of k_1. For the general case, it may be concluded that the rate of the branching-chain reactions depends on the concentrations of both hydrogen and oxygen, and that the degree of dependence is a function of temperature and of composition over all conditions normally encountered in the study of this reaction in the high-temperature, low-pressure region.

ACKNOWLEDGMENTS

This work was supported principally by the U.S. Army Research Office—Durham, and partially by the Robert A. Welch Foundation.

REFERENCES

1. **Schott, G. L. and Kinsey, J. L.**: J. Chem. Phys *29*, 1177 (1958).
2. **Schott, G. L.**: J. Chem. Phys. *32*, 710 (1960).
3. **Kaufman, F. and Del Greco, F. P.**: *Ninth Symposium (International) on Combustion*, p. 659, Academic Press, 1963.
4. **Kondratiev, V. N.**: Kinetika Ximitcheskix Gazovix Reaktsii, Sec. 38, U.S.S.R. Academy of Sciences, 1958. (English translation: Kinetics of Chemical Gas Reactions, AEC–TR–4493, 1961).
5. **Semenov, N. N.**: Some Problems in Chemical Kinetics and Reactivity, Chap. X, Princeton University Press, 1959.
6. **Duff, R. E.**: J. Chem. Phys. *28*, 1193 (1958).
7. **Clyne, M. A. A.**: *Ninth Symposium (International) on Combustion*, p. 211, Academic Press, 1963.
8. **Brokaw, R. S.**: *Analytic Solutions to the Ignition Kinetics of Hydrogen–Oxygen Reaction*, NASA TM X–52003, 1964.
9. **Schott, G. L.**: Private communication, 1964.
10. **White, D. R. and Millikan, R. C.**: J. Chem. Phys. *39*, 1803, 1807, 2107, 3209 (1963).
11. **Carrington, T.**: J. Chem. Phys. *31*, 1418 (1959).
12. **Baldwin, R. R.**: *Ninth Symposium (International) on Combustion*, p. 687, Academic Press, 1963.
13. **White, D. R.**: Private communication.
14. Note added in proof: This form of the solution is for three real roots. Imaginary roots also occur for physically realizable conditions.
15. Note added in proof: We have subsequently determined that the correct threshold for our apparatus is 3×10^{-7} moles/liter. This finding necessitates some revision of the rate coefficient expressions, which will be reported at a later date.

COMMENTS

Dr. M. A. Khan (Shell Research Ltd., Thornton): I would like to ask about the activation energy of the initiation reaction

$$H_2 + O_2 \xrightarrow{E_0} OH + OH.$$

In his well known book *Chemical Kinetics and Chain Reactions*, Semenov quotes $E_0 = 62$ kcal mole^{-1}, a value derived from the Haber mechanism, using Hinshelwoods' data. Again, in 1945, Semenov derived a value of 45 kcal mole^{-1} from Kowalsky's data. We now know that the Haber mechanism is obsolete. Could Gardiner give any reasons for not using the figure of 45 kcal mole^{-1}, and is there really any theoretical or experimental basis for the figure of 70 kcal mole^{-1}, which he uses in his paper?

Prof. W. C. Gardiner, Jr. Very little information about the rate coefficient for homogeneous chain initiation is available, and the assignment $H_2 + O_2 = 2\,OH$, with the rate parameters given in our paper should be regarded only as a reasonable guess. At high temperatures, thermal dissociation of hydrogen, for which reliable rate coefficients are now available [Sutton, E. A.: J. Chem. Phys. *36*, 2923 (1962)], appears to be faster than any other initiation process. Semenov suggests (*Some Problems in Chemical Kinetics and Reactivity*, Vol. 2, p. 151, Princeton University Press, 1959) that the early data of Kowalsky, if interpreted in terms of homogeneous chain initiation, yield an order-of-magnitude rate constant of 10^{-23} for $H_2 + O_2 = 2\,OH$, or $H_2 + O_2 = HO_2 + H$, at 800°K. Belles has interpreted the data of White and Moore (this Symposium, p. 785) for rich mixtures, and finds that 45 kcal appears to be a reasonable activation energy for the initiation step. Hirsch and Ryason [J. Chem. Phys. *40*, 2051 (1964)] find that experimental values for ignition delay can be reproduced computationally with chain initiation via thermal dissociation of hydrogen only, which has an activation energy of 103 kcal. Careful ignition-delay measurements in rich mixtures over a wide temperature range, analyzed with a procedure similar to that used by Dr. Belles, might provide more information on this subject. Lacking more and better data, however, there are no firm grounds for identifying homogeneous initiation with a specific elementary reaction or for assigning an activation energy.