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Kinetic Studies of Hydroxyl Radicals in Shock Waves. II. Induction Times in the Hydrogen-Oxygen Reaction*

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(Received June 13, 1958)

The formation of OH in the shock wave induced combustion of H_2 and O_2 has been measured by oscillographically recording the absorption of ultraviolet OH line radiation. The main features of the reaction course are: (1) an induction period whose length, t_i, varies inversely with $[O_2]$, (2) an increase in the product $[O_2]$ t_i as t_i becomes short compared to the vibrational relaxation time of O_2, and (3) at the end of the induction period, a sigmoid rise of $[OH]$ to a maximum, followed by a slow decrease. t_i has been studied over the ranges: $1100° \leq T \leq 2600°K$, $1.3 \times 10^{-5} \leq [O_2] \leq 8.0 \times 10^{-4}$ mole/l, $0.25 \leq [H_2]/[O_2] \leq 5.$, $0.004 \leq [O_2]/[Ar] \leq 0.20$, and $5 \leq t_i \leq 500$ μsec. Agreement between incident and reflected shock experiments has been demonstrated. According to the branching chain mechanism known from explosion limit studies, t_i is governed by the rate of $H + O_2 \xrightarrow{k_1} OH + O$ according to: $2 k_1 [O_2] t_i = 2.303$ n, where n is the number of decades by which $[OH]$ increases between initiation and the end of the induction period. The values of $[O_2] t_i$, which is nearly proportional to $1/k_1$, are summarized by: $\log_{10}([O_2] t_i)$ (mole l^{-1} sec) $= -10.647 + (3966 \pm 625)/T$. The value $k_1 = 1.4 \times 10^9$ deduced at $1650°K$ from this work is combined with data near $800°K$ to give: $k_1 = 3 \times 10^{11}$ exp$(-17.5 \pm 3$. kcal$/RT)$ (mole/l)$^{-1}$ sec.$^{-1}$. The relation of these results to detonation experiments is discussed.

INTRODUCTION

THE branching chain kinetics of the combustion of hydrogen and oxygen has been studied extensively over the past thirty years in the temperature and pressure regions of the explosion limits.[1] This work has led to several estimates of the rate coefficient[2] and activation energy[3] of the elementary reaction

$$H + O_2 \rightarrow OH + O$$
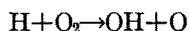
which controls the rate of chain branching.

One property of the branching chain mechanism is the occurrence of an induction period in the explosive reaction. This induction period has been observed manometrically and the rate of chain branching has been measured directly in the explosion peninsula (between the first and second explosion limits in the temperature-pressure plane) near $800°K$.[4-6]

Recent studies of the structure of the reaction zone in H_2—O_2 detonation waves have not shown any

evidence of the expected induction period,[7-9] indicating that it is either absent or too short to be resolved under the experimental conditions used.

In the present investigation, the kinetics of formation of hydroxyl radicals in the shock wave induced combustion of H_2 and O_2 has been examined by measuring oscillographically the absorption of ultraviolet OH line radiation. The experiments have been done at shocked gas temperatures between $1100°$ and $2600°K$. This temperature range is well above the explosion limits, so that combustion proceeds rapidly as a homogeneous gas reaction. While these temperature conditions include those encountered in detonation wave fronts, the present experiments differ from detonation waves in that the H_2—O_2 mixtures are diluted with an excess of argon. This means that the shock waves, which are supported by expanding high-pressure hydrogen, may be varied in strength and that the reaction conditions behind the shock front are nearly isothermal. Also, because the partial pressures of H_2 and O_2 are much lower than are practical in detonations, the reactions are slower and the induction period as well as the approach to equilibrium can be resolved.

The length of the induction period has been studied in detail as a function of temperature and of the H_2, O_2, and inert gas concentrations. The results provide a significant extension of the low temperature rate data and a valuable link between explosion limit experiments and an understanding of detonation wave structure. The outstanding features of the reaction

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[1] The general principles and early work are summarized by, for example, B. Lewis and G. v. Elbe, *Combustion, Flames, and Explosions* (Academic Press, Inc., New York, 1951), Chaps. I and II, and R. N. Pease in *Combustion Processes*, Lewis, Pease, and Taylor, editors (Princeton University Press, Princeton, New Jersey, 1956), pp. 160-174.
[2] R. R. Baldwin and A. D. Walsh, Discussions Faraday Soc. 17, 96 (1954).
[3] D. R. Warren, Proc. Roy. Soc. (London) A211, 106 (1952).
[4] A. Kovalsky, Physik. Z. Sowjetunion 1, 595 (1932); 4, 723 (1933). An account of Kovalsky's experiments, in English, can be found in N. Semenov, *Chemical Kinetics and Chain Reactions* (Oxford University Press, London, 1935), pp. 217-225.
[5] A. Nalbandjan, Acta Physicochim. U.R.S.S. 19, 483 (1944).
[6] Deduction of rate constants from Kovalsky's data has been given by N. Semenov, Acta Physicochim. U.R.S.S. 20, 291 (1945).

[7] G. B. Kistiakowsky and P. H. Kydd, J. Chem. Phys. 25, 824 (1956).
[8] T. Just and H.-G. Wagner, Z. physik. Chem. (Frankfurt) 13, 241 (1957).
[9] W. R. Gilkerson and N. Davidson, J. Chem. Phys. 23, 687 (1955).

course, as observed in these experiments, are: (1) an induction period whose length, t_i, varies inversely with the O_2 concentration, (2) an increase in the product $[O_2]t_i$ as t_i becomes short compared to the vibrational relaxation time of O_2, and (3) at the end of the induction period, a sharp sigmoid rise of the OH concentration which is followed by a maximum and a slow decrease as equilibrium is approached. Quantitative interpretation of this third feature is being pursued and will be reported later.

DESCRIPTION OF EXPERIMENT

The general techniques associated with spectrochemical measurement of reaction rates in shock waves have been described by Davidson and co-workers.[10] In this work, hydroxyl radical concentrations down to 10^{-6} mole/l are measured by absorption of characteristic OH line radiation in the band at 3064 A. The source of this OH radiation is a flash lamp containing water vapor. The details of this technique, including the calibration on equilibrium OH concentrations, and a description of the shock tube equipment have been published in Paper I of this series.[11] The experimental innovations in the present investigation are: (1) piezoelectric crystal gauges[12] to detect the shock wave in measuring its velocity, and (2) an auxiliary beam of visible light in a schlieren arrangement[13] to detect the arrival of the shock front at the optical observation slit.
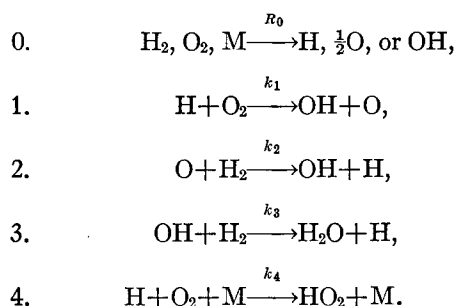
The method of deduction of the temperature behind incident and reflected shock waves has also been considered in paper I. In the present experiments with incident shock waves, the true induction period is of course obtained from the time interval measured on the oscilloscope trace by multiplying by the density

C – MAXIMUM [OH]   A–B, INDUCTION PERIOD
B – EXPONENTIAL RISE   C–on, SLOW APPROACH
A – SHOCK WAVE   TO EQUILIBRIUM

FIG. 1. Sample oscillographic record showing the principal features of the reaction course. OH absorption vs time in shocked H_2+O_2+argon. ($T=1300°$K before reaction and sweep time$=500$ μsec.)

[10] T. Carrington and N. Davidson, J. Phys. Chem. **57**, 418 (1953); Britton, Davidson, and Schott, Discussions Faraday Soc. **17**, 58 (1954).
[11] Bauer, Schott, and Duff, J. Chem. Phys. **28**, 1089 (1958).
[12] H. T. Knight, Rev. Sci. Instr. **29**, 174 (1958).
[13] W. Bleakney in *Physical Measurements in Gas Dynamics and Combustion, Part I*, R. W. Ladenburg, editor (Princeton University Press, Princeton, New Jersey, 1954), pp. 159–163.

ratio of the shock wave, which corrects a stationary observer's time scale for the motion of the gas behind the shock wave.

A sample OH absorption vs time oscillogram of the reaction course is shown in Fig. 1.

BRANCHING CHAIN MECHANISM

The important reaction steps during the induction period are believed to be[6]

0. $\qquad H_2, O_2, M \xrightarrow{R_0} H, \frac{1}{2}O, \text{ or OH},$

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

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

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

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

The steps in the branching chain are the elementary reactions 1, 2, and 3. It is assumed that during the induction period back reactions are negligible and the concentrations of H_2 and O_2 are not diminished from their initial values. Furthermore, since only reaction 1 is significantly endothermic, k_2, $k_3 \gg k_1$, and so long as $[H_2]/[O_2] \gtrsim 1$, reactions 2 and 3 are much faster than reaction 1. The termination reaction, 4, is of no consequence at these high temperatures because it is slow and because HO_2 is unstable. Under these conditions, OH and O atom are steady state intermediates which are used up practically as fast as they are formed and the principal chain carrier is the H atom, whose concentration increases exponentially with time according to

$$d[H]/dt = 2k_1[O_2][H], \qquad (1)$$

$$[H] = [H]_0 \exp\{2k_1[O_2](t-t_0)\}. \qquad (2)$$

Here, t_0 is any reference time following which Eqs. (1) and (2) are valid, and the subscript zero on concentration denotes the value of that concentration at time t_0.

Initiation of the chain may occur directly by the formation of H atoms or indirectly through reactions 2 and 3 by the formation of equivalent amounts of O or OH. The unspecified initiation process is denoted by reaction 0, whose rate, R_0, depends only on the initial reactants and hence is certainly constant over the short time interval before the branching chain becomes established.

It is of interest to define the origin of time, t, for an element of gas as the instant of passage of the shock wave. Then it can be shown that[6] although Eq. (1) does not obtain until some short time after $t=0$, Eq. (2) is effectively obeyed throughout the induction period with t_0 taken as zero and $[H]_0$ taken as that value of $[H]$ which makes the rate of chain branching
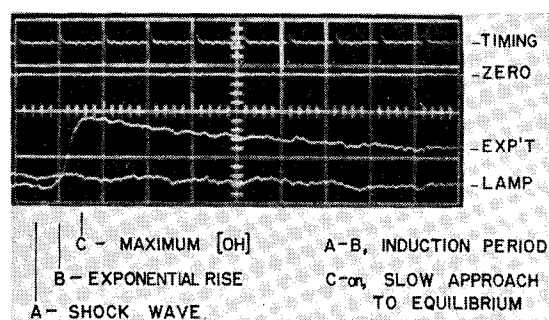
equal to the rate of initiation. Thus

$$2k_1[O_2][H]_0 = R_0. \qquad (3)$$

This point is illustrated in Fig. 2.

The steady state expression for [OH] in terms of [H] is

$$[OH] = [H](2k_1[O_2]/k_3[H_2]) \qquad (4)$$

so that [OH] also increases exponentially according to

$$[OH] = [OH]_0 \exp(2k_1[O_2]t). \qquad (5)$$

$[OH]_0$ is given by Eqs. (3) and (4).

In the present experiments, OH is not detectable until near the end of the induction period. We may define the induction time, t_i, as the time at which the OH concentration reaches the threshold of detectability, approximately 1×10^{-6} mole/l. Calling this concentration $[OH]_i$, we then describe the induction time, t_i, by the equations:

$$[H]_i/[H]_0 = [OH]_i/[OH]_0 = \exp(2k_1[O_2]t_i) \qquad (6)$$

$$n = \log_{10}([OH]_i/[OH]_0) = 0.8686k_1[O_2]t_i. \qquad (7)$$

Equations (1)–(7) are illustrated for a typical set of experimental conditions in Fig. 2. This reaction profile was computed by the numerical integration code described by Duff[14] and using the system of reactions and rate constants assumed by him in studying hydrogen-oxygen detonations. In these computations, initiation occurs primarily by two reactions, the $H_2 + O_2 \rightarrow 2OH$ process assumed at low temperatures by Semenov,[6] and the dissociation of hydrogen, $H_2 + M \rightarrow H + H + M$, which makes significant contributions only above 2000°K. The branching chain sets in quickly and dominates the reaction throughout the remainder of the induction period, until significant amounts of H_2 and O_2 have been consumed and back reactions become important. After the induction period, a maximum occurs in the computed H, O, and OH concentrations, followed by a slow approach to equilibrium controlled by three-body recombination processes. The present measurements of OH concentrations *vs* time clearly verify this general picture of the reaction course.

The computation described by Fig. 2 indicates that the experimental value $[OH]_i = 1 \times 10^{-6}$ mole/l is reached before [OH] departs significantly from Eq. (5). Also, since n is fairly large (about 7 in the hypothetical case of Fig. 2), its estimation is relatively insensitive to inaccuracy in the estimation of $[OH]_0$. On the basis of the constants and reactions assumed in reference 14, the estimated values of n are between 3 and 10 for the ranges of conditions covered in the present experiments. The principal variation in n is with temperature, and it is substantially independent of the concentrations over the ranges covered. Thus the product $[O_2]t_i$ is expected to depend only on
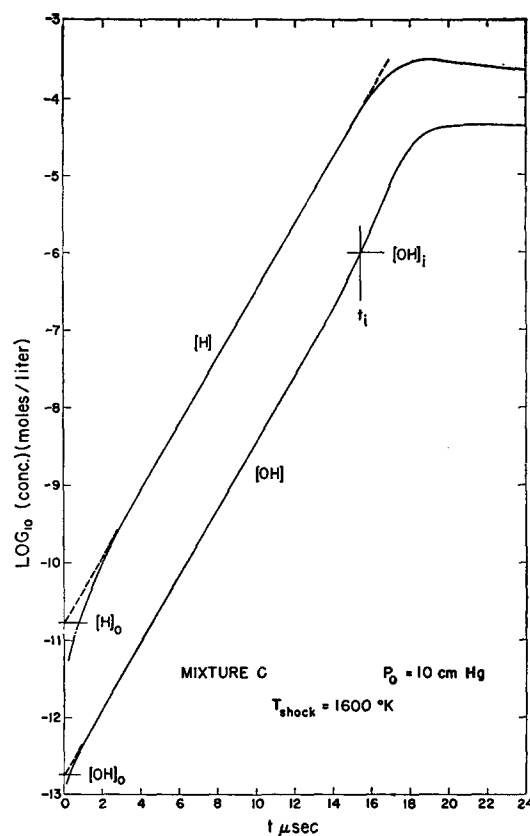
14 R. E. Duff, J. Chem. Phys. **28**, 1193 (1958).

FIG. 2. Hypothetical reaction course (computed) for 4% $H_2 + 2\%O_2$ in Ar (the approximate composition of mixture C), showing the details of the induction period and illustrating Eqs. (1)–(7). The values of $[H]_0$ and $[OH]_0$ indicated by extrapolation are indistinguishable from those calculated from Eqs. (3) and (4).

temperature and to vary with temperature approximately as $1/k_1$, so that a plot of $\log([O_2]t_i)$ *vs* $1/T$ should be approximately linear.

RESULTS AND CONCLUSIONS

Measurements of $[O_2]t_i$

Experiments have been done with eight mixtures of H_2 and O_2 in Ar. The compositions of these mixtures, determined mass spectrometrically, and the ranges of conditions covered with each mixture are summarized in Table I.

The induction time results for mixtures $A - F$ are presented in Fig. 3 as $\log([O_2]t_i)$ *vs* $1/T$. The anticipated simple linear relationship is approximately obeyed over the temperature range $1100° \leq T \leq 2600°K$, and there is general agreement, within experimental scatter, among the results obtained with the three different $[H_2]/[O_2]$ ratios. The points enclosed in the rectangle near 1650°K cover the seventeen-fold range of O_2 concentration $1.3 \times 10^{-5} \leq [O_2] \leq 22. \times 10^{-5}$ mole/l. From the approximate constancy of the product $[O_2]t_i$ over this range, it can be seen that Eq. (7) is satisfactorily obeyed. The experiments in incident and reflected shock waves also give equivalent results, thus

TABLE I. Summary of experimental conditions.

Mixture	A	B	C	D	E	F	H	H'	All
Type of shock	Incident	Incident	Incident	Incident	Incident	Reflected	Incident	Incident	
No. of experiments	13	25	27	12	17	13	7	3	117
$\%O_2$	0.43	0.49	1.99	0.45	2.00	0.49	19.7	4.0	0.4–20
$[H_2]/[O_2]$	1.6	2.0	1.9	5.5	0.5	2.0	0.25	0.25	0.25–5.5
Temp. range °K (approximate)	1400–2500	1400–2300	1300–2300	1400–2500	1100–1800	1800–2600	1600–1900	1750–1850	1100–2600
$[O_2]$ Range in shock (mole/l)$\times 10^5$	1.6–4.0	1.3–5.3	7.0–22.0	2.1–7.8	11.0–40.0	4.7–32.0	20–80	37.0	1.3–80

supporting the general validity of the methods, at least under these conditions of shock strength and argon pressure.

The line in Fig. 3, fitted by least squares, is described by

$$\log_{10}([O_2]t_i) \text{ (mole } l^{-1} \text{ sec)}$$
$$= -10.647 + (3966 \pm 625)/T. \quad (8)$$

The uncertainty indicated in the coefficient of $1/T$ is the probable error (50% confidence level) from the least squares analysis. The indicated temperature

dependence of $([O_2]t_i)^{-1}$ corresponds to a value of 18.1±2.9 kcal/mole for the approximate activation energy of reaction 1.

Vibrational Relaxation Effects

In general, the preceding results confirm the simple predictions of the branching chain mechanism. However, a more careful analysis of the data reveals some inconsistencies. First, if one attempts to evaluate k_1 and its associated activation energy by estimating n over the temperature range of the experiments, one observes that while $[O_2]t_i$ changes by a factor of about
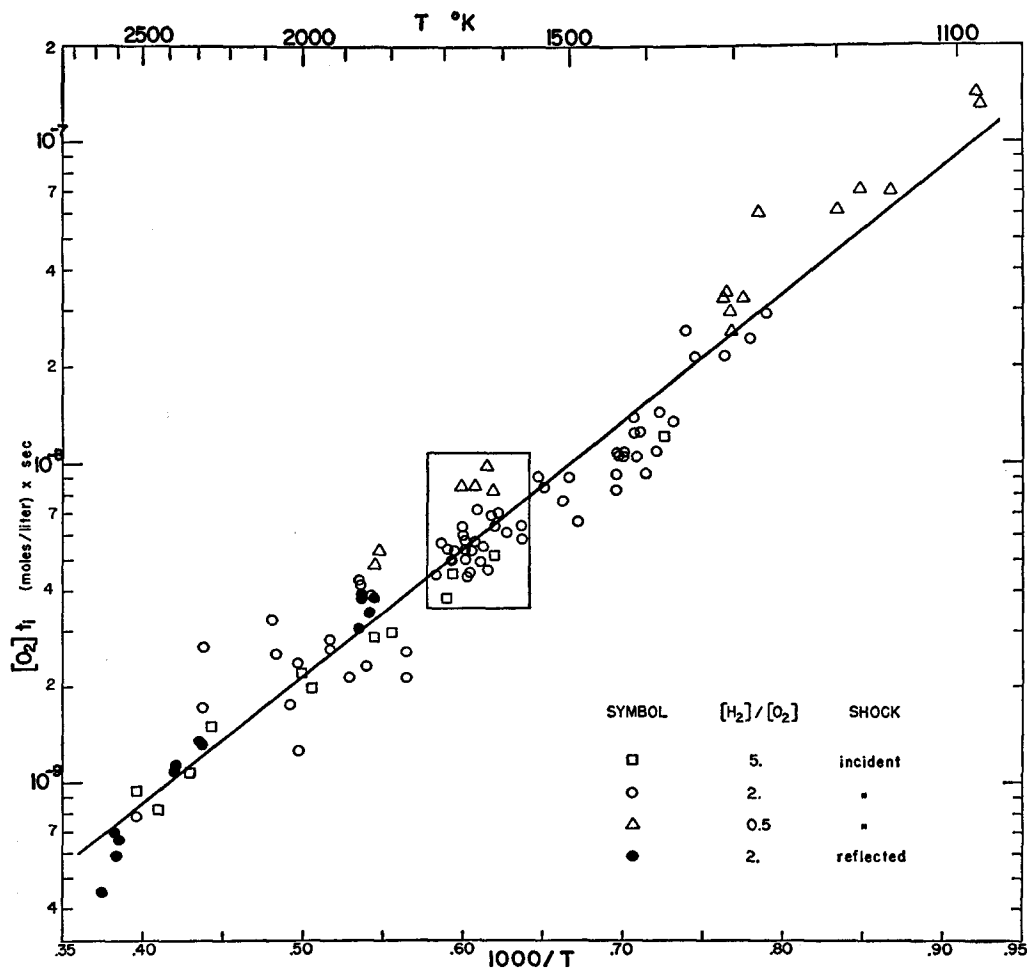

FIG. 3. Plot of induction time data showing the dependence of $[O_2]t_i$ on temperature and comparing results for different experimental mixtures and shock wave techniques. The line through the points is Eq. (8).

100 between 1100° and 2600°K, n changes by about a factor of three, so that the indicated activation energy of reaction 1 is not 18 kcal/mole, but more like 13 kcal/mole. This value is unreasonably low in view of the data on the temperature coefficient of the second explosion limit which lead to values between 17 and 28 kcal/mole for this activation energy,[3] and in view of the fact that reaction 1 is endothermic by 16 kcal/mole.

A second difficulty is seen as a systematic difference between the values of $[O_2]t_i$ obtained in the various mixtures in the neighborhood of 1800°K. This is shown in Table II, in which it is seen that mixtures C and E, which contain 2% O_2, give higher values of $[O_2]t_i$ than the mixtures containing 0.5% O_2. This trend is confirmed by the additional experiments in mixtures H and H', which were done to test the effect of still larger O_2 percentages. While the evidence is not un-equivocal, it appears that the trend of increasing $[O_2]t_i$ is associated primarily with increasing mole fractions of O_2, and not with variation of the density, the H_2/O_2 ratio, or the H_2 mole fraction.

Both these difficulties can be understood qualitatively when one observes that in all the experiments above 2000°K and in the oxygen-rich mixtures at temperatures down to about 1700°K the measured induction times, t_i, are not long compared to the vibrational relaxation time of O_2.[15] This suggests that under these conditions reaction 1 takes place in vibrationally cold O_2 for a sizable fraction of the induction period and hence the average value of k_1 is less than the thermal equilibrium value.

This hypothesis is supported by the data in Table II. The values of $[O_2]t_i$ listed at 1800°K were evaluated for each mixture from least squares expressions of the form of Eq. (8). The probable errors in these values have not been computed precisely; graphical inspection indicates that they are all about ±30%. Also listed in Table II are the values of the ratio of the length of the induction period, t_i, to the vibrational relaxation time of O_2, τ_{vib}, for each mixture. The values of τ_{vib}, the reciprocal of the first order rate coefficient for vibrational relaxation, were taken from Blackman's measurements[15] in pure O_2, and hence are not strictly applicable to the present mixtures in which the principal constituent is Ar. However, Blackman's results on the effects of N_2 and H_2O on the vibrational relaxation of O_2 at high temperatures indicate that different gaseous environments do change τ_{vib} markedly. The present tabulation is intended only to show the approximate range of t_i/τ_{vib} covered by the experiments. The details of the variation of $[O_2]t_i$ with t_i/τ_{vib} remain to be investigated thoroughly. The present results serve only to identify tentatively the nature of the effect and to indicate the limited range of validity of Eq. (8) and the magnitude of observed deviations from it.

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[15] V. Blackman, J. Fluid Mech. **1**, 61 (1956).

TABLE II. Variation of $[O_2]t_i$ at 1800°K with %O_2 and t_i/τ_{vib}.

Mixture	%O_2	%H_2	$[O_2]t_i$ at 1800°K mole l^{-1} sec$\times 10^9$	t_i/τ_{vib}
A	0.4	0.7	2.7	12.0
B	0.5	1.0	3.7	14.0
D	0.5	2.5	3.1	11.0
F	0.5	1.0	4.5[a]	13.0
C	2.0	3.8	4.7	4.3
E	2.0	1.0	5.4	5.0
H'	4.0	1.0	7.8	3.6
H	20.0	4.9	11.7	1.1

Eq. (8) (average based on Fig. 3, mixtures H, H' not included) — 3.6

[a] Because of the uncertainty in temperature deduction in re-flected shock waves before chemical reaction, this figure, which is based on the assumption of equilibrium at the reflecting surface, represents an upper limit to $[O_2]t_i$ at 1800°K. See reference 11.

Estimation of n and k_1

Ideally, it should be possible to determine k_1 by Eq. (5) from the shape of the OH absorption vs time curves near the end of the induction period, as was done in the low temperature manometric experiments.[4,6] The present records are not accurate enough to do this reliably, however, because of the appreciable noise in the photoelectric signal and the low level of absorption at which the OH concentration obviously departs from Eq. (5).

The other approach to n and k_1 is to deduce $[OH]_0$ by estimation of the initiation rate, R_0. Then, since $[OH]_i$ is known, Eq. (7) gives n and k_1 from the measured $[O_2]t_i$. Because of the exponential growth of the chain, an order of magnitude uncertainty in $[OH]_0$ corresponds to an uncertainty of only one unit in n, and hence to only a small fractional uncertainty in k_1.

This procedure has been followed at 1650°K, where $[O_2]t_i$ has been most extensively measured and where it is believed that the results represent the thermal equilibrium value of k_1, essentially free of complications from the vibrational condition of the oxygen. It may be noted that the initiation reactions are almost certainly governed by conditions of incomplete vibrational relaxation in all of the present experiments, but because of the exponential nature of the branching chain process, this effect on t_i is small. If we assume that, at 1650°K, the principal initiation reaction is

$$H_2+O_2 \xrightarrow{k_0} 2OH,$$
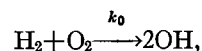
with the estimated[14] rate coefficient $k_0 = 1 \times 10^{11}$ exp$(-70.$ kcal$/RT)$ (mole/l)$^{-1}$ sec^{-1}, then, from Eqs. (3) and (4), $[OH]_0 = 2k_0[O_2]/k_3$. Assuming[14] $k_3 = 3 \times 10^{11}$ exp$(-2.5$ kcal$/RT)$ (mole/l)$^{-1}$ sec^{-1}, and taking $[OH]_i = 1 \times 10^{-6}$ mole/l and a typical value of $[O_2]$ as 5×10^{-5} mole/l, we have $n = 7.1$. From Eq. (8), $[O_2]t_i$ at 1650°K is equal to 5.7×10^{-9} mole l^{-1} sec, and then from Eq. (7), $k_1 = 1.43 \times 10^9$ (mole/l)$^{-1}$ sec^{-1}.

Correlation with Low-Temperature Results

To determine the activation energy of reaction 1, we may combine the foregoing result with the value $k_1 = 5 \times 10^6$ (mole/l)$^{-1}$ sec^{-1} at 793°K recommended by Baldwin and Walsh.[2] This leads to the Arrhenius expression,

$$k_1 = 3 \times 10^{11} \exp(-17.5 \text{ kcal}/RT) \text{ (mole/l)}^{-1} \text{ sec}^{-1}. \quad (9)$$

Consideration of possible uncertainties of a factor of 2 in the values of k_1 at 1650° and 793°K leads to an uncertainty of ± 3 kcal/mole in this activation energy.

The activation energy given in Eq. (9) agrees with the lower of the many estimates that have been made.[3] It is in good agreement with the result given by Semenov,[6] who deduced an activation energy of about 18 kcal/mole from the values of k_1 near 800°K by equating the pre-exponential factor to the collision rate coefficient. Thus it is clear that an activation energy significantly higher than 18 kcal/mole would be unreasonable because an abnormally large pre-exponential factor would be required.

Several careful studies of the temperature dependence of the second explosion limit under conditions remote from the junctions with the first and third limits have been interpreted as indicating that $(E_1 - \text{``}E_4\text{''})$ is between 20 and 23 kcal/mole.[3] The present results show that E_1 is almost certainly less than 20 kcal/mole. Thus k_4, like other termolecular recombination rate constants, is seen to decrease with increasing temperature. This temperature dependence of k_4 is confirmed by the findings of Hoare and Walsh,[16] who describe k_4 by a "negative activation energy" of "E_4" ≈ -4 kcal/mole. In assessing the agreement or disagreement among the above numbers, one must keep in mind that the temperature dependence of the second limit tends to correspond to an activation energy that is greater than $(E_1 - \text{``}E_4\text{''})$. As Warren has pointed out,[3] this is because of the effects of surface destruction of the primary chain carriers at lower temperatures and chain regeneration and/or second order branching at higher temperatures, and different authors may slightly overcorrect or undercorrect the activation energy in taking these effects into account.

Application to Detonations

The present results contribute to an understanding of several observations that have been made on hydrogen-oxygen detonations and related systems. First, the induction period does exist under the temperature conditions of detonation waves, but it is short compared to the approach to equilibrium which follows it. At the end of the induction period, during which the branching chain mechanism predominates, the chain reactions 1–3 come effectively to a balanced state of partial equilibrium. At this point the mechanism changes abruptly to one in which progress is measured by the comparatively slow recombination of excess atoms and OH radicals. This description of the reaction zone is consistent with the measurements of density[7] in H_2—O_2 detonation fronts, in which a finite reaction zone but no detectable induction period is observed. The recent measurements of OH concentrations in detonations[8] likewise confirm this picture by demonstrating the presence of excess OH which disappears as equilibrium is approached. Similar excesses of H and OH have been observed in the gases leaving the reaction zone in H_2—O_2 flames.[17] Thus the overshoot of atom and radical concentrations is not peculiar to shock and detonation phenomena, but is a property of the branching chain mechanism.

From the values of $[O_2]t_i$ given by Eq. (8), the induction times under detonation conditions can be computed, and it has been shown[14] that the predicted values are in the submicrosecond range and are indeed less than the resolving time of the experiments that have been done.

Since it is known that t_i is greater than given by Eq. (8) when vibrational relaxation is not relatively fast, the induction times predicted for detonations may be too short. Further work is needed on this subject, particularly to determine the effectiveness of H_2, which is very efficient at low temperatures,[18] in promoting vibrational relaxation of O_2 at high temperatures.

[16] D. E. Hoare and A. D. Walsh, Trans. Faraday Soc. 53, 1102 (1957).

[17] Bulewicz, James, and Sugden, Proc. Roy. Soc. (London) A235, 89 (1956).

[18] H. O. Kneser and V. O. Knudsen, Ann. Physik Ser. 5 21, 682 (1935).