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Shock-Tube Study of the Hydrogen–Oxygen Reaction. II. Role of Exchange Initiation

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An extended analytical solution to the rate equations for the branching-chain reactions of the H_2–O_2 reaction under shock-tube conditions is presented. Together with an experimental determination of the detection threshold for OH of the Bi (3067) line-absorption method used in earlier experiments, this solution allows quantitative comparison of calculated and experimental ignition delays. It is shown that calculation and experiment can be brought into agreement with slight modification of chain-reaction rate coefficients deduced from the results of other studies of the H_2–O_2 reaction. The essential role of the rate of chain initiation by a path other than diatom dissociation in determining the ignition delays is brought to light. Rate-coefficient expressions for the chain reactions are suggested and supported.

CHEMICAL kinetics studies of combustion reactions have always been more qualitative than quantitative in nature due to the facts that these reactions tend to involve many intermediate species and are usually very sensitive to experimental conditions. Thus, while combustion kinetics studies have yielded some insights into reaction pathways, actual rates of the elementary reactions involved are only slowly becoming known. The hydrogen–oxygen reaction, however, is an apparent exception to this situation. Here the number of possible chemical species and the number of elementary reactions interconverting them are small, and some of these reactions may also be investigated under wide ranges of conditions far removed from those of the usual combustion studies. In recent years quantitative rate studies of almost all the possible elementary reactions, in some cases achieved by investigating the reverse reaction to the elementary step of importance in combustion, have accumulated to the point that one may place as much confidence in the rate coefficients deduced for them as one may place in any gas kinetics results. It is particularly gratifying that Arrhenius expressions for the rate coefficients for several of the important steps can give satisfactory agreement with data taken from widely different kinds of experiments and over wide ranges of $1/T$. Thus it appears that the hydrogen–oxygen reaction, prototype of the branching-chain explosion, may soon be understood both qualitatively and quantitatively. However, there still remain experimental conditions, for example, the shock-wave-induced reaction near the second limit of explosion, where quantitative rate studies are difficult; there remain uncertainties in the relative importances of the several pathways for radical recombination and chain initiation; and the rate-coefficient expressions for the elementary reactions must be subjected to further adjustments as additional experiments are done. In this paper we report an extensive analysis of earlier shock-tube induction-time data obtained by OH absorption measurements. We show that changes of the Arrhenius parameters found to give satisfactory fits to other experimental data are necessary in order to fit the shock-tube data, and that chain initiation by a reaction other than diatom dissociation plays a far greater role in determining the induction times than heretofore assumed.

We have occasion to refer to data obtained by a variety of methods, some of them involving experimental conditions where many elementary reactions besides those considered here may be important. The experimental data with whose analysis we are primarily concerned, however, were taken in incident shock waves under what may be called the low-pressure, high-temperature, high-dilution conditions (0.2–0.5 atm, 1400–2500°K, 96%–98% Ar) obtained by shocking 10 mm of test gas containing $H_2/O_2/Ar$ percentages of 1/3/96, 1/1/98, and 3/1/96.[1] Here the shock-tube technique is free from disturbances which may affect data taken under other conditions and here the rate equations for the induction period of the hydrogen–oxygen explosion can be cast in a simple yet complete form. The kinetic scheme describing the early stages of the shock-induced reaction has been discussed from theoretical and experimental points of view before[2–6]; we present it here without detailed justification.

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* U.S. Public Health Service Predoctoral Fellow.

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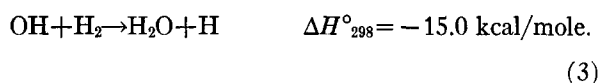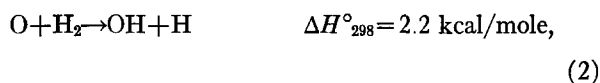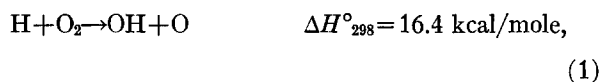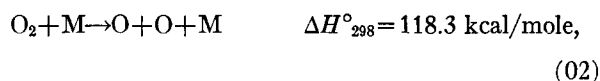
[3] G. L. Schott, J. Chem. Phys. 32, 710 (1960).

[4] V. N. Kondratiev, *Kinetika Ximitcheskix Gazovix Reaktsii* (U.S.S.R. Academy of Sciences, 1958) Sec. 38 [English translation: *Chemical Kinetics of Gas Reactions* (Pergamon Press, Inc., New York, 1964), Sec. 39].

[5] N. N. Semenov, *Some Problems in Chemical Kinetics and Reactivity* (Princeton University Press, Princeton, New Jersey, 1959), Chap. 10.
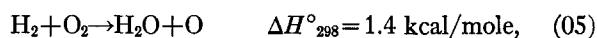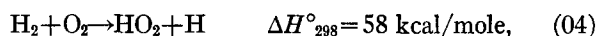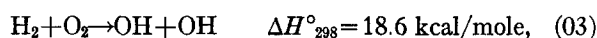
[6] F. E. Belles and M. R. Lauver, Symp. Combust. 10th, Cambridge, England, 1964, 285 (1965).

We have to consider the set of reactions

$$H_2+O_2 \rightarrow O, H, \text{ or } OH \tag{00}$$

$$H_2+M \rightarrow H+H+M \qquad \Delta H°_{298}=104.2 \text{ kcal/mole,} \tag{01}$$

$$O_2+M \rightarrow O+O+M \qquad \Delta H°_{298}=118.3 \text{ kcal/mole,} \tag{02}$$

$$H+O_2 \rightarrow OH+O \qquad \Delta H°_{298}=16.4 \text{ kcal/mole,} \tag{1}$$

$$O+H_2 \rightarrow OH+H \qquad \Delta H°_{298}=2.2 \text{ kcal/mole,} \tag{2}$$

$$OH+H_2 \rightarrow H_2O+H \qquad \Delta H°_{298}=-15.0 \text{ kcal/mole.} \tag{3}$$
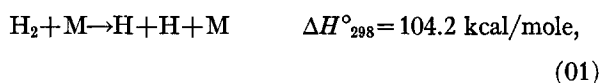
We refer to Reactions (00)–(02) as initiation reactions, Reactions (1)–(3) as chain reactions. Initiation by dissociation of reactant molecules certainly occurs; the rate coefficients are moreover known independently from direct measurements in the shock tube. Whether or not the reaction suggested in (00) occurs to a significant extent has not been proved; we argue later that it does in fact play a major role, and that its rate may be deduced from the induction-period data. Although we may deduce the rate of this reaction, we cannot identify it with the present experimental data. Of the three possibilities

$$H_2+O_2 \rightarrow OH+OH \qquad \Delta H°_{298}=18.6 \text{ kcal/mole,} \tag{03}$$

$$H_2+O_2 \rightarrow HO_2+H \qquad \Delta H°_{298}=58 \text{ kcal/mole,} \tag{04}$$

$$H_2+O_2 \rightarrow H_2O+O \qquad \Delta H°_{298}=1.4 \text{ kcal/mole,} \tag{05}$$

the first two would seem preferable to the last one from simple geometry. If HO_2 is stable in the temperature range of interest here, then the second reaction is in effect an oxygen-catalyzed thermal dissociation of hydrogen and its rate could be taken into account together with the rate of (01) in a manner described below. If HO_2 decomposes rapidly by reaction with H_2, then (04) becomes $2H_2+O_2 \rightarrow H_2O+H+OH$, and its rate would contribute both to (01) and (03). The first reaction is unique among the initiation reactions in having OH as a product. The identity of the chain center first produced is not important in the kinetics, since the chain reactions rapidly change the molecular identity of the chain center. Reactions (03)–(05) are then kinetically indistinguishable in the sense that they are bimolecular reactions between H_2 and O_2 to produce chain centers. For incorporation into the differential equations describing the growth of chain-center concentration, however, only the first reaction involves an addition to the equations, since H and O production in initiation are already present from (01) and (02). We therefore assign the process (03) as the only exchange-

initiation pathway, and drop (04) and (05) from further consideration. If the conclusion from the formal analysis of this paper is true, that exchange initiation plays an important role in determining the induction times, then positive identification of the products of this reaction becomes quite an interesting challenge to combustion kinetics.

ANALYTICAL SOLUTION OF RATE EQUATIONS

The system of differential equations is similar to that investigated previously by Stubbeman[7] and others.[8–10] We add the two terms arising from the dissociation reactions of O_2 and H_2, and extend the solution to allow for the occurrence of complex roots. The rate equations are

$$d[OH]/dt=[H][O_2]k_1+[O][H_2]k_2 \\ -[OH][H_2]k_3+2[H_2][O_2]k_{03},$$

$$d[O]/dt=[H][O_2]k_1-[O][H_2]k_2+2[O_2][M]k_{02},$$

$$d[H]/dt=[O][H_2]k_2+[OH][H_2]k_3 \\ -[H][O_2]k_1+2[H_2][M]k_{01}.$$

These simultaneous differential equations may be solved for the experimental conditions of interest here by the operator technique, since during all but the very last part of the induction period, when Reactions (01)–(3) are no longer adequate to describe the reaction system, the concentrations of hydrogen and oxygen remain constant. The start of the deviation of our analytical solution from a numerical integration of the rate equations for all the relevant reactions will occur well after the end of the induction period for all experimental conditions for which we have data.

The operator form of the rate equation is

$$(D+c)x-za-yb=2R_{03},$$

$$(D+b)y-za=2R_{02},$$

$$(D+a)z-yb-xc=2R_{01},$$

where x, y, and z are [OH], [O], and [H], respectively, and $a=[O_2]k_1$, $b=[H_2]k_2$, and $c=[H_2]k_3$, $R_{01}=[H_2][M]k_{01}$, $R_{02}=[O_2][M]k_{02}$, and $R_{03}=[H_2][O_2]k_{03}$. The auxiliary equation is the same for all three solutions

$$D^3+(a+b+c)D^2+bcD-2abc=0.$$

The particular solutions are $x_p=-2(R_{01}+R_{02})/c$, $y_p=-(R_{03}+R_{01})/b$, and $z_p=-(R_{03}+R_{01}+2R_{02})/a$.

The cubic auxiliary equation may have three real and unequal roots, three real roots of which two are equal, or one real and a pair of conjugate-complex roots, depending on the discriminant of the cubic equa-

[7] R. F. Stubbeman, dissertation, The University of Texas, Austin, 1963.
[8] Reference 4. pp. 517–520 (English transl.: pp. 614–617).
[9] G. L. Schott and J. H. Kiefer (personal communication).
[10] R. S. Brokaw, Symp. Combust. 10th, Cambridge, England, 1964, 269 (1965).

tion. The improbable condition that the discriminant is zero, yielding two real and equal roots, is not considered. The solutions have a different form depending on whether the roots are real or complex; both must be considered, since the sign of the discriminant changes for the rate coefficients and experimental conditions with which we have to deal. For real roots the solutions are of the form

$$x = c_{1x} \exp(B_1 t) + c_{2x} \exp(B_2 t) + c_{3x} \exp(B_3 t) + x_p.$$

The relationships between the constants c_{ia} in the expressions for x, y, and z may be found by substituting into the original equations and equating coefficients.[7] For complex roots, the solution for y may be written

$$y = c_{1y} \exp(B_1 t) + c_{2y} \exp(B_2 t) \cos B_3 t$$
$$+ c_{3y} \exp(B_2 t) \sin B_3 t + y_p.$$

To evaluate the constants for this solution a different approach must be used. Similar solutions may be derived for x and z in terms of the constants c_{1y}, c_{2y}, and c_{3y} by substituting into the original differential equations. We then have three equations for x, y, and z in terms of the three constants c_{iy}, the three roots of the auxiliary equation, and the time. The initial conditions x, y, $z = 0$ at $t = 0$ suffice to determine the constants c_{1y}, c_{2y}, c_{3y}, as in the real-root case discussed in our previous paper.

The final result is a very complicated but explicit expression for the OH concentration as a function of time which may be solved by iteration to determine the time required to reach a specified OH concentration. This complete solution was programmed for a Control Data Corporation 1604 computer. The input consists of trial rate coefficient expressions, the OH detection threshold, compositions of experimental H_2-O_2-Ar mixtures, the starting pressure for the shock-tube experiments, the temperature range of interest, and the high-temperature molar enthalpies of H_2, O_2, and Ar. Pressures behind the incident shock waves which achieve these temperatures are computed with conventional methods and used to find the concentrations of O_2 and H_2 behind the waves. Induction times are computed for each composition and temperature and plotted as $\log[O_2] \times t_i$ versus $10\ 000/T$ by the CDC 165 plotter.[11]

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[11] The use of $[O_2] \times t_i$ as induction-time parameter was introduced by Schott and Kinsey (Ref. 2) as the result of a partial-steady-state treatment of Reactions (1)–(3). It has since been found that the partial-steady-state approximation is clearly inappropriate for O under the experimental conditions we consider here, and it is probably not suitable for O either at these temperatures except for H_2-rich mixtures. We retain the multiplication by $[O_2]$ in order to scale the induction-time data with reactant concentration so that the effects of changing H_2:O_2 ratio and temperatures are displayed on the output graphs. The geometrical mean $[H_2]^{\frac{1}{2}}[O]^{\frac{1}{2}}$ has also been used as scaling parameter [D. R. White and G. E. Moore, Symp. Combust. 10th, Cambridge, England, 1964, 785 (1965)]. However, this choice only has theoretical significance for part of the range of H_2:O_2 ratios studied, and it tends to bring the induction-time data for mixtures with different H_2:O_2 ratio together, which is not desired here.

The output graphs may be used for comparison of calculated and experimental induction times, or compared with one another to find the effects of changes in the input rate coefficient expressions upon the computed induction times.

DETERMINATION OF OH DETECTION THRESHOLD

The raw experimental data we desire to interpret consist of oscilloscope-trace photographs showing the variation with time of the anode current of the photomultiplier monitoring the intensity of the Bi(3067) beam traversing the shock tube.[1] In most of the experiments discussed here, velocity gauge signals were also recorded on the same photographs in order that the time of shock passage at the observation station would be recorded together with the photomultiplier signals. The induction time is then experimentally defined as the time interval between shock passage and the first detectable decrease in Bi(3067) intensity, multiplied by the shock density ratio. Under the most favorable conditions used, the residual uncertainty in measuring this time interval is about 2 μsec laboratory time, comprised in about equal measure of uncertainty due to noise in the photomultiplier signal and uncertainty of shock arrival time. The raw output of the analytical solution to the rate equations is OH concentration as a function of gas time. Our problem now is to correlate the experimentally defined induction time with its corresponding point on the OH concentration versus time curve.

Ideally this could be accomplished in two direct ways. One could measure the emitting and absorbing line shapes and use the known oscillator strength of OH to obtain an extinction coefficient, or one could measure the transmission of gas with known OH concentration for the Bi(3067) line.[12] Unfortunately, the lamps we built were too unstable to permit the first alternative, and we did not have equipment available for the usual procedures for realizing the second. In our shock tube it would be possible to generate shocks in which chemical equilibrium would be attained and maintained for suitable lengths of time and in which the OH concentration would be in a suitable range. Such experiments could not be done under conditions close to those of the induction-time experiments, however, since the temperature would have to be substantially higher, and the influence of OH line-shape change on the deduced extinction coefficient would be a question. We chose rather to utilize existing experimental records from induction-time experiments.[7] In these experiments chemical equilibrium is never attained, except at the highest temperatures, since the pressures are so low that termolecular recombination reactions are too slow to bring the gas to chemical equilibrium within the limited observation time. Instead, a condition of partial

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[12] G. L. Schott and P. F. Bird, J. Chem. Phys. 41, 2869 (1964).

equilibrium is attained, where the forward and reverse rates of Reactions (1)–(3) become equal without minimizing the free energy of the gas. This instance of constrained equilibrium was discussed in detail by Schott.[3] The partial equilibrium condition is just as well defined as the total equilibrium condition and for the experimental conditions used here is an excellent approximation that can be used just as well for calibration purposes. Moreover, the additional advantage is gained that calibration and induction-time experiments are done under identical conditions.

The partial equilibrium condition is specified by the equilibrium constants for Reactions (1)–(3), the conservation of matter balances

$$[O_2]_0 = [O_2] + \tfrac{1}{2}[O] + \tfrac{1}{2}[OH] + \tfrac{1}{2}[H_2O],$$

$$[H_2]_0 = [H_2] + \tfrac{1}{2}[H] + \tfrac{1}{2}[OH] + [H_2O],$$

and the requirement that the average number of atoms per molecule remain 2

$$[H_2O] = [H] + [O].$$

The subscript zero denotes conditions after passage of the shock wave but before onset of reaction. Six equations are available to solve for the six unknown concentrations. Since the set cannot be solved explicitly, we reduced it to the two equations

$$[O_2]_0 = (\{([H]+[O])[O]K_2\}/K_3)^{\tfrac{1}{2}}$$
$$\times \{([O]/[H]K_1) + \tfrac{1}{2}\} + [O] + \tfrac{1}{2}[H]$$

and

$$[H_2]_0 = (\{([H]+[O])[O]K_2\}/K_3)^{\tfrac{1}{2}}$$
$$\times \{([H]/[O]K_2) + \tfrac{1}{2}\} + \tfrac{3}{2}[H] + [O],$$

solved this pair by iteration, and thence computed the partial equilibrium concentration of OH. The equilibrium-constant expressions recommended by Kaufman and Del Greco[13] were used

$$K_{-1} = 3.33 \times 10^{-3} T^{0.372} \exp(17.13/RT),$$

$$K_{-2} = 0.44 \exp(1.87/RT),$$

$$K_3 = 0.21 \exp(15.19/RT).$$

A program for this computation was combined with a program for computing incident-shock parameters, so that the starting pressure, experimental gas composition, and shock velocity could immediately be correlated with the partial equilibrium concentration of OH.

This procedure contains an approximation which requires justification. The temperature and pressure assigned to each computation are those of the Hugoniot curve for the incident shock wave with no chemical reaction. A small amount of heat is released in the chain reactions, however, and the temperature of the

gas actually rises. To show that this heating does not have a substantial effect upon the calculation, let us compare the error in computed shock velocity with the change in shock velocity required for a 100-deg increase in temperature and from this estimate the error in the partial equilibrium concentration of OH.

A typical situation would be an 1800°K shock wave in a mixture of $H_2:O_2:Ar = 1:1:98$ and a starting pressure of 10 mm Hg. The shock velocity required, allowing no reaction, is 1322.0 m/sec at 1800°K and 1364.2 m/sec at 1900°K. Shocking to a total equilibrium condition at 1800°K requires a shock velocity of 1281.7 m/sec. The true partial-equilibrium shock velocity will fall somewhere between these extremes and may be calculated utilizing a total-equilibrium computational routine by reducing the starting pressure until a synthetic partial-equilibrium condition is reached where $[H_2O] = [H] + [O]$.[3] This condition will give the partial-equilibrium shock velocity since this velocity is independent of the starting pressure. The partial-equilibrium shock velocity is 1321.5 m/sec. The difference between the no-reaction shock velocity and the true partial-equilibrium velocity is only 0.5 m/sec as opposed to a change of 42.2 m/sec required to go from 1800° to 1900°K. Since this represents only about 1-deg error in temperature it may be seen that heat release in the reaction can be neglected and that our use of the no-reaction shock conditions is justified.

The transmission of the Bi(3067) radiation from our lamp was measured at partial equilibrium from a large number of induction-time oscillograms. The percent transmission is plotted versus computed partial equilibrium concentration of OH in Fig. 1. When analyzing a typical oscillogram to obtain an induction time a trace deflection of about 1 mm or slightly less is significant, whereas the total deflection from $I=0$ to $I=I_0$ may be about 50 mm. The concentration of OH has thus made a significant change in the recorded photomultiplier signal at 98% transmission. Due to the short extrapolation used in smoothing the noise on the trace, the actual transmission corresponding to the end

[13] F. Kaufman and F. P. Del Greco, Symp. Combust. 9th, Ithaca, New York, 1962, 177 (1963).
  Note added in proof: H. Wise, C. M. Ablow, and K. M. Sancier [J. Chem. Phys. **41**, 3569 (1964)] find $k_3 = 6 \times 10^6$ liter/mole·sec at 300°K, in excellent agreement with the value of Kaufman and Del Greco.
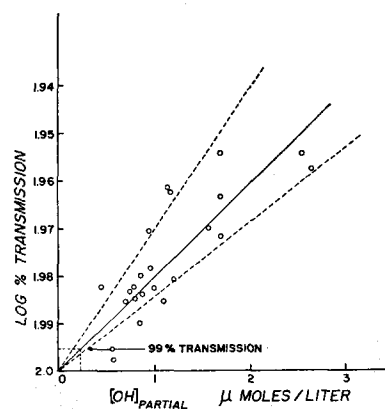

FIG. 1. Determination of OH detection threshold from extrapolation of percent transmission vs partial equilibrium OH concentration to 99% transmission.

of the induction period may be even somewhat more. The upper and lower lines of Fig. 1 give reasonable limits for extrapolating the data to 100% transmission. If we arbitrarily choose 99% transmission as the cutoff, the [OH] cutoff is seen to be about 0.25 μmole/liter. It is shown later that an approximate value of the [OH] cutoff is sufficient for our purposes here; the effect of reasonable variations of [OH] cutoff on computed induction times is shown to be small.

CORRELATION WITH EXPERIMENTAL DATA

In fitting calculated ignition-delay curves to the experimental data it is important to study in addition to the effects of adjusting the rate coefficients for the chain reactions, the effects of inclusion, exclusion, and varying the rate of the exchange-initiation process. The contributions of the two dissociation reactions to chain initiation are readily calculated, since the thermal dissociations of hydrogen and oxygen have been studied by numerous investigators using shock-tube methods. It is shown that calculated ignition delays are too long if recommended Arrhenius fits to experimental values for the various rate constants are used; to make a token effort to shorten them, we deliberately choose the dissociation rate coefficients rather on the high side of the available experimental scatter.[14] Ar, O_2, and H_2 are considered as collision partners for dissociation. The rate expressions used are

$$R_{01} = ([Ar]+[O_2]+4.1[H_2])[H_2]10^{11.79}$$
$$\times \exp(-103.24/RT),$$
$$R_{02} = ([Ar]+9[O_2])[O_2]10^{15.56}T^{-1}\exp(-118.0/RT)$$

in units of moles per liter per second. Initiation by dissociation is included in all computations reported here.

We first calculate the delay profiles using Arrhenius expressions that have been recommended by authors who fitted data from studies in various temperature ranges, with various experimental methods[2,13,15-26]; these
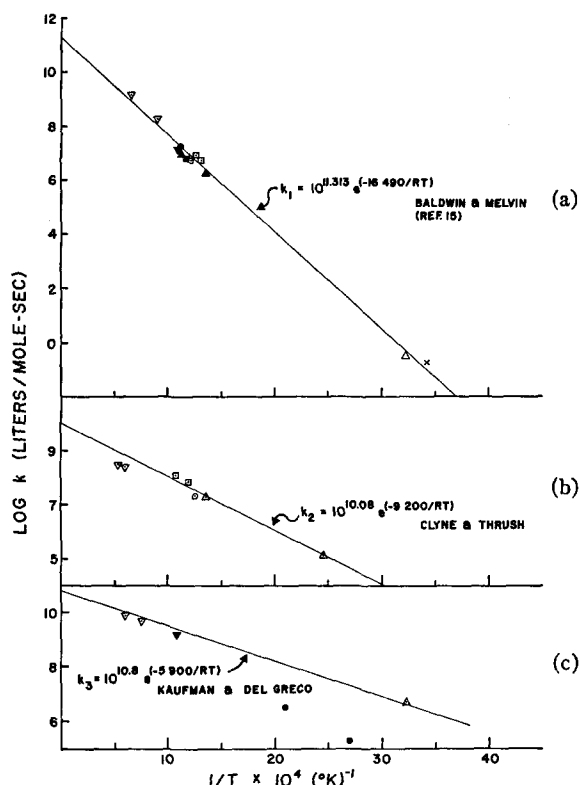
[14] The thermal dissociations of O_2 and H_2 have been studied in the shock tube by numerous authors. We use values for the O_2 dissociation rate constant taken from M. Camac and A. Vaughan, J. Chem. Phys. **34**, 460 (1961), and values for the H_2 dissociation rate constant taken from E. Sutton, J. Chem. Phys. **36**, 2923 (1962).

[15] R. R. Baldwin and A. Melvin, J. Chem. Soc. **1964**, 1785.

[16] M. A. A. Clyne and B. A. Thrush, Nature **189**, 135 (1961).

[17] M. A. A. Clyne, Symp. Combust. 9th, Ithaca, New York, 1962, 211 (1963).

[18] R. R. Baldwin and D. W. Cowe, Trans. Faraday Soc. **52**, 1344 (1956).

[19] L. V. Karmilova, A. B. Nalbandyan, and N. N. Semenov, Zh. Fiz. Khim. **32**, 1193 (1958).

[20] C. P. Fenimore and G. W. Jones, J. Phys. Chem. **63**, 1154 (1959).

[21] V. V. Azatyan, V. V. Voevodskii, and A. B. Nalbandyan, Kinetics and Catalysis (USSR) (Engl. Transl.) **2**, 315 (1961) [Kinetica i Kataliz **2**, 340 (1961)].

[22] R. R. Baldwin, Trans. Faraday Soc. **52**, 1344 (1956).

[23] C. P. Fenimore and G. W. Jones, J. Phys. Chem. **65**, 993 (1961).

[24] L. I. Avramenko and R. V. Lorentso, Zh. Fiz. Khim. **24**, 207 (1950).

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

[26] G. Dixon-Lewis, M. M. Sutton, and A. Williams, Symp. Combust. 10th, Cambridge, England, 1964, 495 (1965).

FIG. 2. Rate constants for Reactions (1)-(3) and "standard" Arrhenius expressions of authors indicated. These graphs are reproduced in subsequent figures to illustrate the assumed changes in rate constants. (a)—[$\triangle$ Kaufman and Del Greco (Ref. 13), $\times$ Clyne (Ref. 17), $\boxdot$ Semenov (Ref. 27), $\odot$ Baldwin and Cowe (Ref. 18), $\blacktriangle$ Karmilova (Ref. 19), $\triangledown$ Fenimore and Jones (Ref. 20), $\blacksquare$ Azatyan (Ref. 21), $\bullet$ Kurzius (Ref. 25), $\blacktriangledown$ Dixon-Lewis, Sutton, and Williams (Ref. 26)]. (b)—[$\triangle$ Clyne and Thrush (Ref. 16), $\odot$ Baldwin (Ref. 22), $\boxdot$ Azatyan (Ref. 21), $\triangledown$ Fenimore and Jones (Ref. 23)]. (c)—[$\triangle$ Kaufman and Del Greco (Ref. 13), $\triangledown$ Fenimore and Jones (Ref. 23), $\bullet$ Avramenko and Lorentso (Ref. 24), $\blacktriangledown$ Dixon-Lewis, Sutton, and Williams (Ref. 26)].

are referred to as "standard" rate coefficients. For k_1 we use the expression $10^{11.313}\exp(-16\,490/RT)$ liter/mole·sec recommended by Baldwin and Melvin[15]; for k_2 we use the expression $10^{10.08}\exp(-9200/RT)$ liter/mole·sec recommended by Clyne and Thrush[16]; for k_3 we use the expression $10^{10.8}\exp(-5900/RT)$ liter/mole·sec recommended by Kaufman and Del Greco.[13] These Arrhenius fits, together with the data on which they are based, are plotted in Fig. 2.

We first calculate the delay curves for the "standard" with initiation by dissociation only, and compare them with the experimental data (Fig. 3). It is plainly evident that something is lacking. The calculated induction times are much too long, the slope is too great, and the lines are too close together. Either the rate coefficients must be changed, the exchange-initiation step included, or both.

As a second attempt to fit the experimental data we use the "standard" rate coefficients for the chain reactions, but this time include H_2-O_2 exchange initiation. If we want to assume that this reaction does occur, we
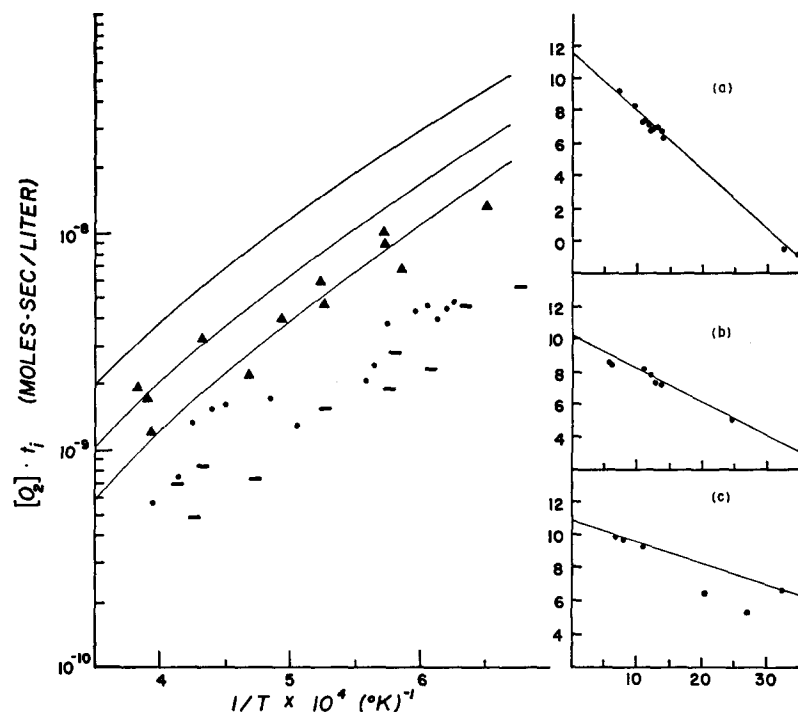
FIG. 3. Calculated induction-time curves for "standard" rate coefficients, excluding exchange initiation, compared to experimental induction times for three mixtures. In this figure and hereafter, the top, middle, and bottom lines represent hydrogen/oxygen/argon percentages of 1/3/96, 1/1/98, and 3/1/96, respectively, and preshock pressure of 10 mm; the triangles, dots, and dashes are the corresponding experimental points (cf. Ref. 1). [(a)—k_1, (b)—k_2, (c)—k_3.]

need an estimate of its rate coefficient. Semenov[5] has estimated a rate constant of $10^{-1.22}$ liter/mole·sec at 800°K based on data of Kovalsky and an assumption of homogeneous chain initiation. We use this as one data point, vary the activation energy over a reasonable range to vary the rate, and observe the effect on the computed delay curves. The results are shown in Fig. 4. Again, we are clearly unable to fit the experimental

data. For exchange-initiation rate coefficients which give the correct slope, the induction times are too long. If we increase the rate, then the high-temperature induction times become unreasonably small. Also, in all cases, the spread of the curves is too small. We reach the same conclusion even if we disregard Semenov's 800°K point and assume a rate differing from his at this temperature by several orders of magnitude. We
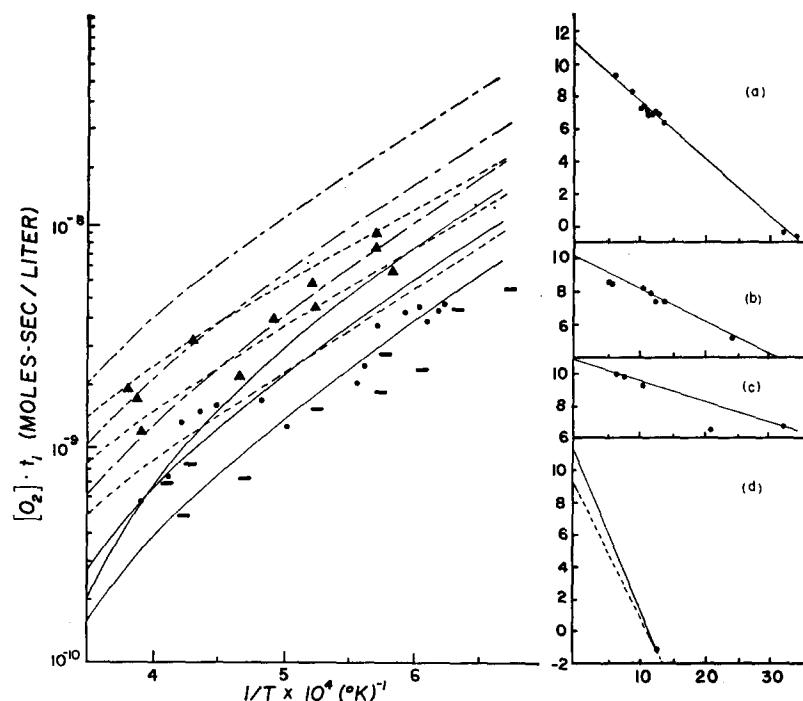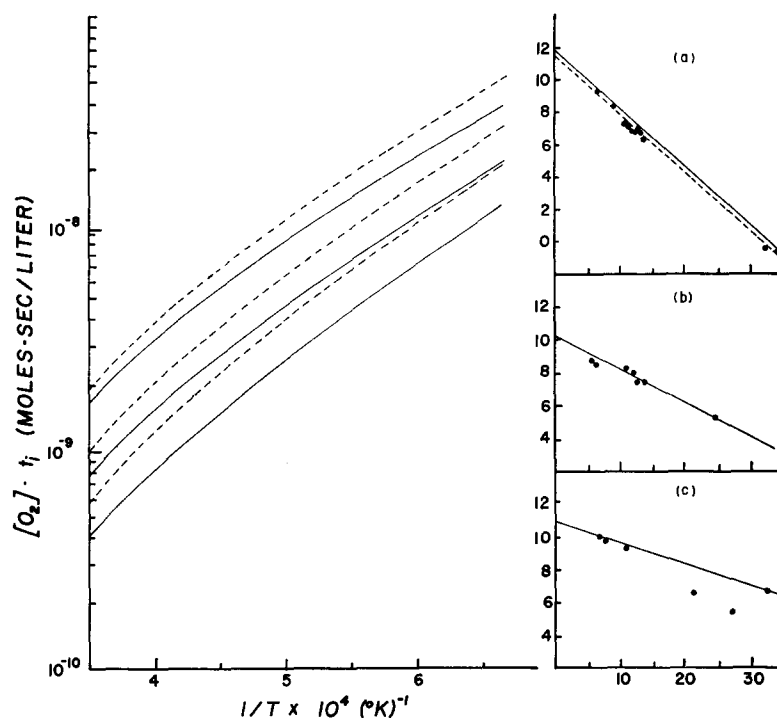

FIG. 4. Delay curves calculated using "standard" coefficients. Effect of including the exchange-initiation reaction. [(a)—k_1, (b)—k_2, (c)—k_3, (d) k_{03}, ------$k_{03}=0$.]

FIG. 5. Sensitivity of delay curves to a twofold increase in k_1, while holding k_2 and k_3 constant. [(a)—k_1, (b)—k_2, (c)—k_3.]

conclude that it is also necessary to modify the rate coefficients for the chain reaction from the "standard" literature values.

SENSITIVITY OF COMPUTED CURVES TO RATE COEFFICIENTS

We next investigate the effects of varying k_1, k_2, and k_3, individually, without including exchange initiation, to observe the resulting changes in the computed curves. For analyzing the effects of k_1, k_2, and k_3 we use the "standard" values for two rates while varying the third. For economy of space, we present but one each of the many variations computed, and then summarize the effects verbally. The results of increasing k_1, k_2, and k_3 by indicated variations of the Arrhenius expressions are shown in Figs. 5, 6, and 7, respectively.

FIG. 6. Sensitivity of delay curves to a twofold increase in k_2, while holding k_1 and k_3 constant. [(a)—k_1, (b)—k_2, (c)—k_3.]
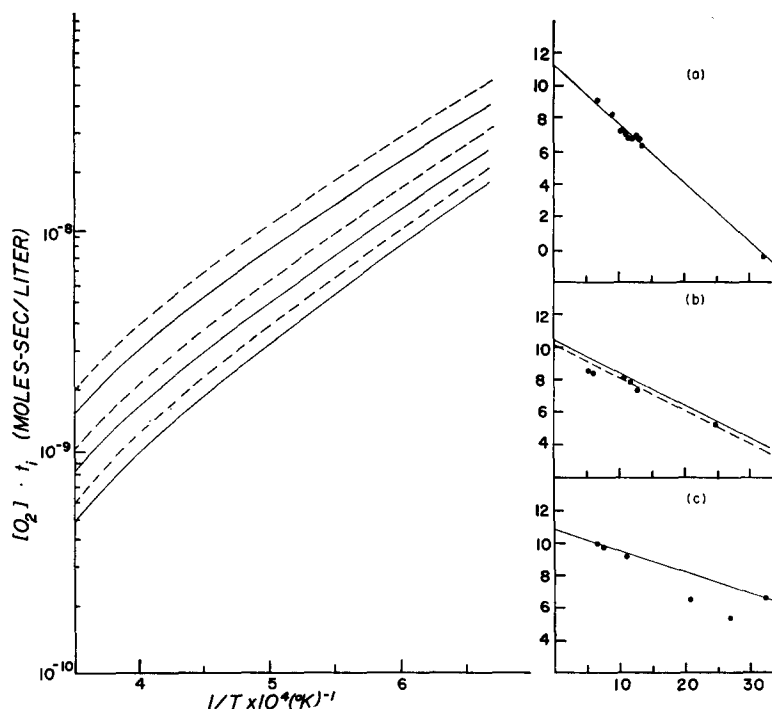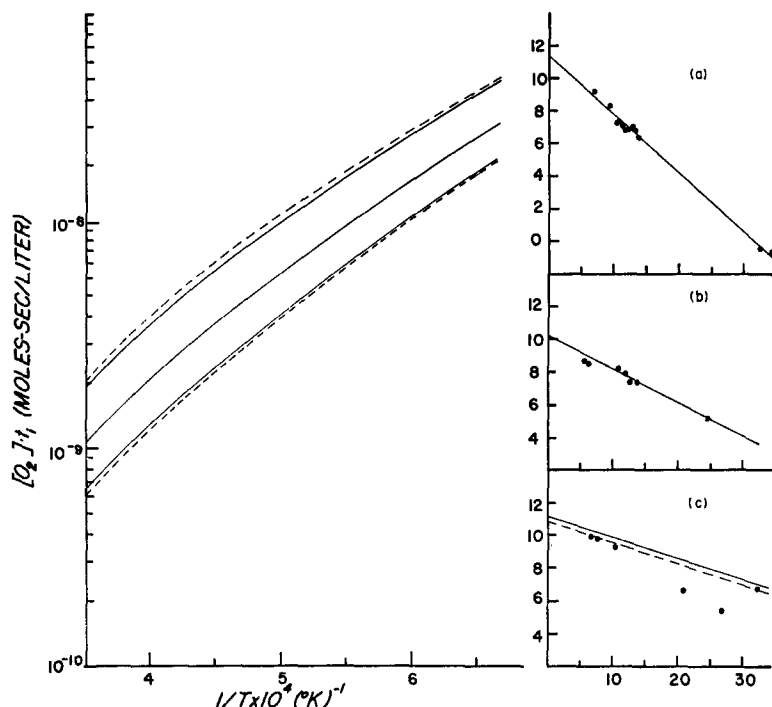
FIG. 7. Sensitivity of delay curves to a twofold increase in k_3, while holding k_1 and k_2 constant. [(a)—k_1, (b)—k_2, (c)—k_3.]

Varying k_1 has a greater effect on the curves than varying either k_2 or k_3. Increasing k_1 causes a decrease in the induction time, particularly for the richer mixtures, a small decrease in the slope, and an increase in the spread of the lines due to the greater decrease in induction time for the rich mixtures.

Increasing k_2 has less effect on the delay curves than increasing k_1, as shown in Fig. 6. Increasing k_2 decreases the induction times and the spread of the curves a small amount, but has little effect on the slope of the lines.

Changing the value of k_3 has little effect on the delay curves for rich mixtures, since it is already faster than either k_1 or k_2. Increasing k_3 does decrease the induction time for the lean mixtures, and thus decreases the spread of the lines, but has no noticeable effect on the slope of the lines.

The effects depicted in Figs. 5, 6, and 7 arose from doubling the pre-exponential factor in the Arrhenius expressions. A second series of calculations was carried out using Arrhenius expressions formed by accepting the "standard" rate constants at room temperature and increasing the activation energies so as to double the rate constants at 2000°K. The resulting delay curves are virtually identical to Figs. 5, 6, and 7.

The sensitivity to increasing the exchange-initiation step is also important, as we later see that it is necessary to include this reaction in the mechanism. This study is complicated by the fact that only one uncertain experimental point is available. If we examine the effect of changing k_{03} by again referring to Fig. 4, we see that the effects of increasing k_{03} are not straightforward. In

general, the induction times and slopes are decreased with little change in the spread of the lines. The important point for present purposes is that the slope can be decreased by adding exchange initiation with the byproduct of lower induction times.

It is fortunate for this analysis that these effects are sufficiently different for each reaction to allow determination of a unique set of rate coefficients which give computed results matching the experimental data.

COMPARISON WITH EXPERIMENTAL DATA

Having determined the effects of varying the chain-reaction rate coefficients, we next use these results to modify the "standards" to try to fit the experimental OH induction times. This was first attempted without including exchange initiation. It is possible to achieve induction times which are short enough by using quite high values of k_1 and k_2; however, even with these high, and, when considered together with rate coefficients deduced from other experiments, quite unreasonable rate coefficients, we are still unable to match the experimental data very well, as shown in Fig. 8. The only way to improve the fit by decreasing the slopes without including the exchange-initiation step is to increase k_1, which is already very large. If k_1 is increased to decrease the slopes, the calculated induction times are too short. We require a means of decreasing the slope, with a smaller effect on the spread of the lines and the absolute induction time. The only possibility is including the exchange-initiation process.

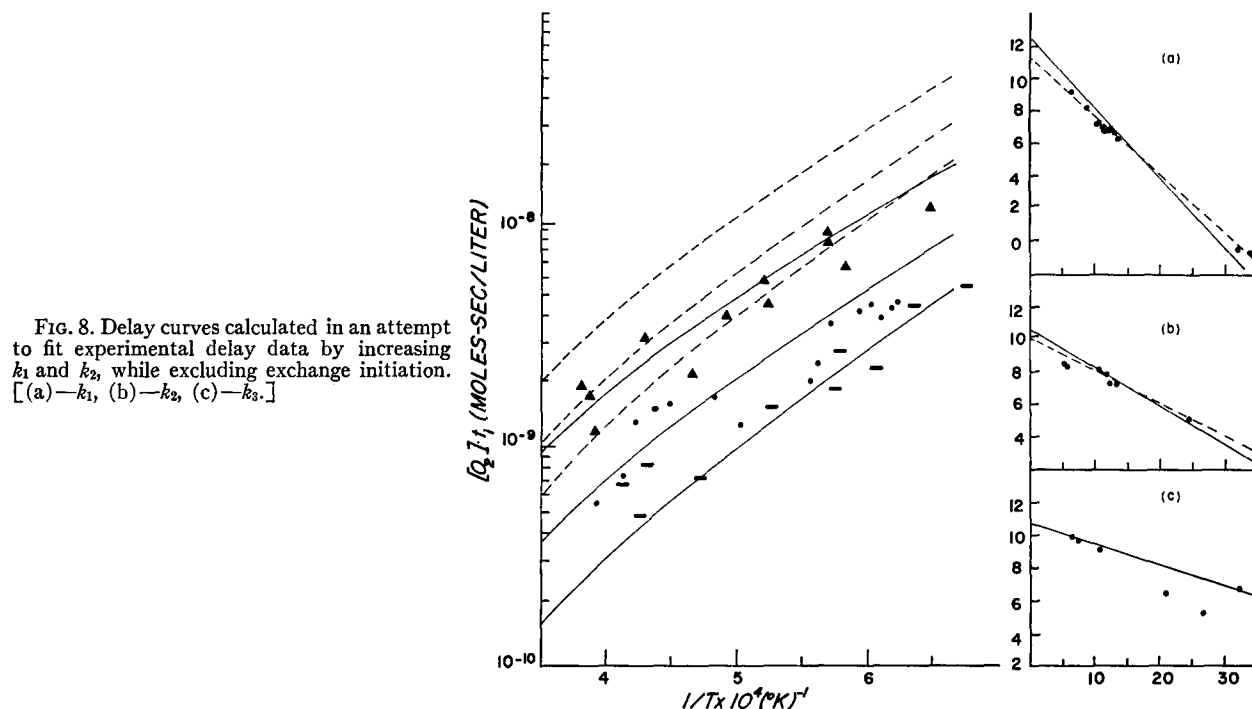It is not possible to obtain a good fit to the experimental data by varying the branching-chain rate co-

FIG. 8. Delay curves calculated in an attempt to fit experimental delay data by increasing k_1 and k_2, while excluding exchange initiation. [(a)—k_1, (b)—k_2, (c)—k_3.]

efficients without including the exchange-initiation step, and we have previously shown that we cannot fit the data using the "standard" coefficients, and varying the rate coefficient for exchange initiation k_{03} alone (Fig. 4). Thus, we conclude that it is necessary not only to include the exchange-initiation mechanism, but also to modify the "standard" rate coefficients, in order to obtain a good fit to the experimental data.

We then made numerous computations to determine a set of chain-reaction rate coefficients and the Arrhenius expression for the exchange initiation required to match the experimental data. The best set was found to be

$$k_{03} = 10^{9.4} \exp(-39\,000/RT),$$

$$k_1 = 10^{11.9} \exp(-17\,600/RT),$$

$$k_2 = 10^{10.08} \exp(-9200/RT),$$

$$k_3 = 10^{10.6} \exp(-5700/RT),$$

in units of liters per mole per second. The computed curves using these coefficients are compared with the experimental data in Fig. 9.

COMPARISON WITH RECOMMENDED ARRHENIUS EXPRESSIONS

The rate coefficient expressions found for k_1, k_2, k_3 are in reasonable agreement with the experimental rates of these reactions determined by various investigators and methods as shown in Fig. 10. The Arrhenius expres-

sion for k_1, although considerably above the expression derived by Baldwin and Melvin[15] by a statistical analysis of all the data points, is not high at all when compared to the high-temperature rates found by Fenimore and Jones.[20] Our rate at 1500°K, 2.2×10^9 liter/mole·sec, is in good agreement with their value at that temperature, 1.44×10^9. The extrapolation to low temperatures
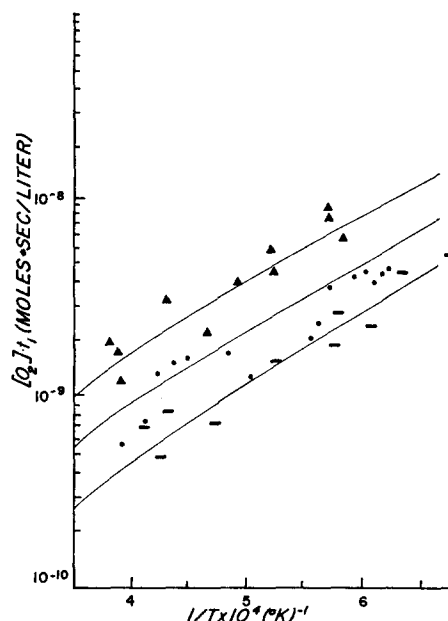

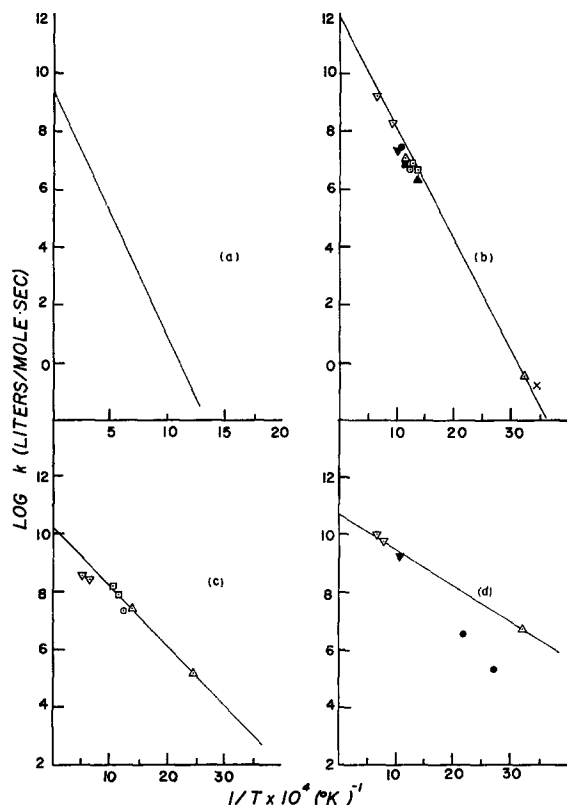FIG. 9. Calculated delay curves for rate coefficients giving the best fit to experimental data.

FIG. 10. Arrhenius expressions giving the best fit to experimental data, as shown in Fig. 11. [(a)—k_{03}, (b)—k_1, (c)—k_2, (d)—k_3.]

gives exact agreement with the rate constant at 310°K determined by Kaufman and Del Greco,[13] and our rate expression agrees in fact very well with that of Kaufman and Del Greco in the temperature range between 1500° and 2500°K.

The expression derived for k_2 is in agreement with the expression of Clyne and Thrush[16] and close to the rates found by Azatyan[21] and by Baldwin.[22] However, the rates measured by Fenimore and Jones[23] are considerably lower than the rates we deduce.

Our Arrhenius expression for k_3, $10^{10.6}$ exp($-5650/RT$) liter/mole·sec agrees quite well with the rates measured by Fenimore and Jones[23] at 1300°–1500°K, and Kaufman and Del Greco[13] at 310°K. The Arrhenius expression derived by Kaufman and Del Greco, $10^{10.8}$ exp($-5900/RT$) liter/mole·sec, does not give as good a fit, but our expression is well within the limits of error set by them.

The Arrhenius expression derived for k_{03} cannot be compared with any experimental point other than that at 800° suggested by Semenov.[27] The pre-exponential factor of $10^{9.4}$ indicates a steric factor of approximately 10^{-2}, which may be considered reasonable for a reaction such as this. The activation energy, 39 kcal, likewise

[27] N. N. Semenov, Acta Physicochim. 20, 290 (1945).

appears reasonable. Other rate expressions for this reaction have been used in data analysis. The expression 10^{11} exp($-70\,000/RT$) liter/mole·sec used by Duff[28] and by Schott and Kinsey[2] and the expression $10^{11.398}$ exp($-67\,000/RT$) liter/mole·sec used by Skinner and Ringrose[29] have no experimental basis, and they clearly cannot be used to obtain a fit of our data, in addition to being lower at 800° than the suggestion of Semenov by a factor of about 10^8. The activation energy estimated by Hirshfelder's[30] rules is approximately 62 kcal. Semenov's estimated activation energy of 45 kcal is based on his rate at 800°K and an assumed theoretical frequency factor.

SENSITIVITY OF RESULTS WITH EXCHANGE INITIATION INCLUDED

We now redetermine the sensitivity of the curves to changes in k_1, k_2, k_3, and k_{03} for the derived set of rate coefficients to show that our original deductions are still valid with the exchange-initiation reaction included and to estimate the accuracy of our approach for calculating these rate coefficients. To do this we use the expressions derived above for three of these coefficients and vary the fourth. We retain the derived activation energy and increase the pre-exponential term of the rate expression by a factor of 2, thus increasing the rate the same amount over the entire temperature range. The results are shown in Figs. 11 and 12. Clearly, effects of this size can be observed, and errors due to the finite sensitivity of the solutions to changes in the rate expressions do not constitute a major defect of our approach.

It may be noted that variations of k_2 and k_{03} produce similar displacements of the delay curves (Figs. 11 and 12). It is, in fact, possible to obtain a good fit of the data by doubling our final k_{03}, and halving our final k_2. Further increase of k_{03}, however, leads to sharp lowering of the delay curves at high temperatures.

EFFECT OF ERROR IN OH THRESHOLD CONCENTRATION ESTIMATE

We now determine what change an error in the specified [OH] detection threshold will introduce into the calculated curves. To do this, we make three calculations for sets of input data identical except for the specified [OH] threshold. We choose upper and lower limits of 0.1 and 1.0 μM/liter, corresponding to observable changes in absorption at 99.5% and 96% transmission, respectively (Fig. 1). The results for these extremes are compared with the results for the assumed value of 0.25 μM/liter in Fig. 13.

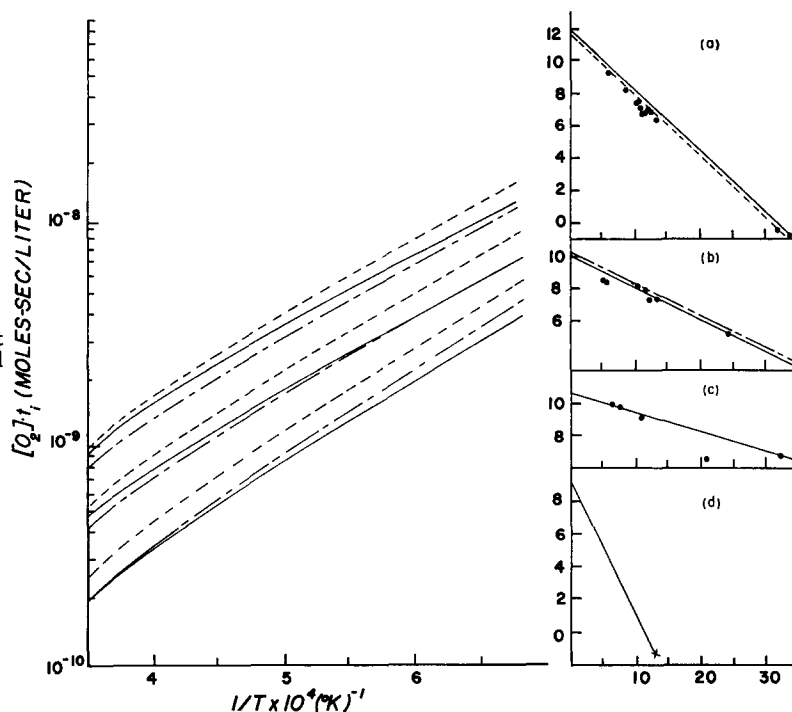[28] R. E. Duff, J. Chem. Phys. 28, 1193 (1958).

[29] G. B. Skinner and G. H. Ringrose, J. Chem. Phys. 42, 2190 (1965); 43, 4129 (1965).

[30] J. O. Hirschfelder, J. Chem. Phys. 9, 645 (1941).

Fig. 11. Sensitivity of delay curves for best rate coefficients to twofold increases of k_1 and k_2. [(a)—k_1, (b)—k_2, (c)—k_3, (d)—k_{03}.]

OH CONCENTRATION PROFILE DURING THE INDUCTION PERIOD

To illustrate the role played by the exchange-initiation rate in determining the ignition delay, we consider OH concentration profiles for the first 75 μsec of re-action. At first we have initiation by Reactions (01), (02), and (03), and the chain-center concentration increases linearly until the branching-chain character is established, as evidenced by the transition to exponential rate of growth of [OH]. Profiles calculated for 1–1–98 mixture of H_2–O_2–Ar, for 1800°, 2100°, and

Fig. 12. Sensitivity of delay curves for best rate coefficients to twofold increases of k_3 and k_{03}. [(a)—k_1, (b)—k_2, (c)—k_3, (d)—k_{03}.]
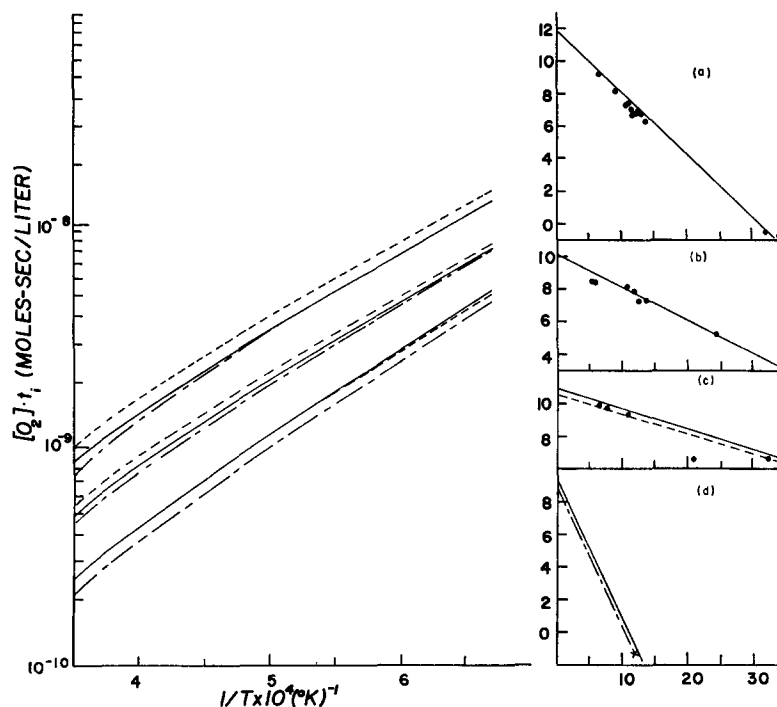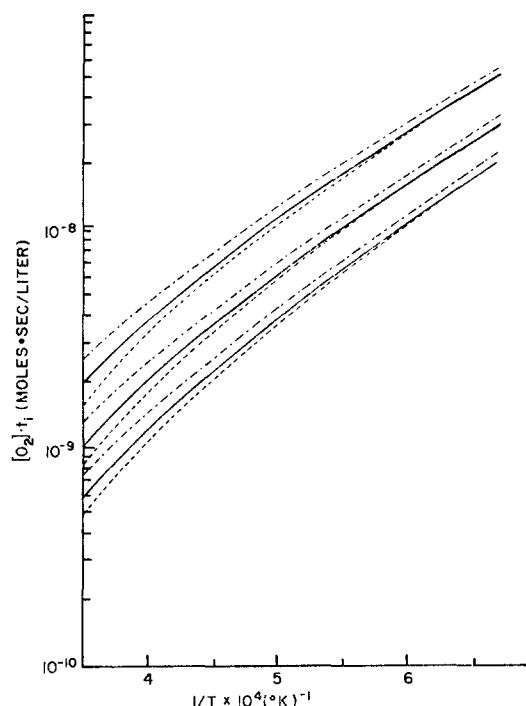
FIG. 13. Effect on delay curves of changing the [OH] detection threshold from 0.25 (——) to 0.1 (– – – –) and 1.0 (—·—·—) μmole/liter.

FIG. 14. OH concentration profiles showing the effect of the exchange initiation reaction on the growth of OH during the first 75 μsec of the induction period. – – – –, including exchange initiation; ——, excluding exchange initiation.

2400°K, are displayed in Fig. 14. The exchange-initiation process was included in calculating one set of profiles and excluded in the other.

The increase in concentration of OH, and of the other chain centers as well, becomes exponential after a time that is determined by the relative rates of the initiation and branching processes. While the slope of this exponential part is nearly independent of the presence or absence of the exchange-initiation process at all three temperatures, the OH concentration when the OH growth becomes exponential may be seen to be quite dependent upon the presence or absence of the exchange-initiation process. Since the exponential growth rates are nearly identical, it is the difference in chain-center concentration at the transition to exponential growth that provides the contribution of the exchange-initiation rate to determining the induction time.
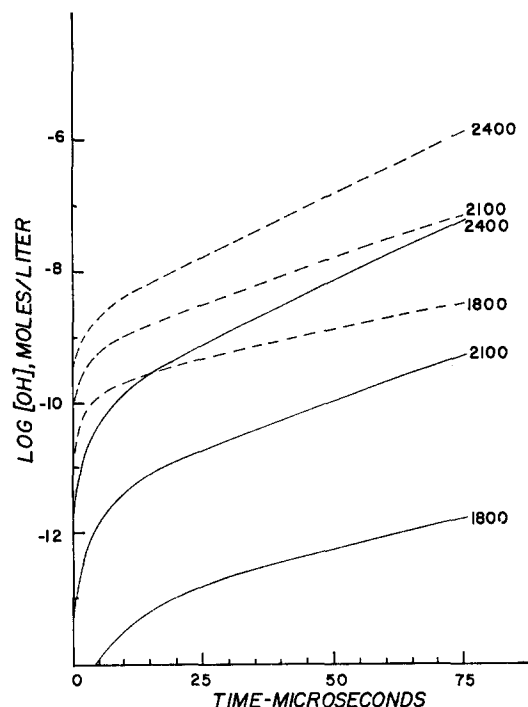
As has long been understood, the initiation rate indeed dominates the rate of increase of chain-center concentration during but a small portion of the total induction period. Furthermore, the length of what might be called the initiation period is not changed by more than a few microseconds by the presence or absence of the exchange-initiation process. However, the effect of the initiation rate is propagated right to the end of the induction period by the value of the chain-center concentration at which chain-center growth becomes exponential. It is this feature of the induction-period kinetics which allows conclusions about the initiation rate to be drawn from induction-time measurements.

ACKNOWLEDGMENTS