

Kinetic Studies of Hydroxyl Radicals in Shock Waves. V. Recombination via the $\text{H}+\text{O}_2+\text{M}\rightarrow\text{HO}_2+\text{M}$ Reaction in Lean Hydrogen—Oxygen Mixtures

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Citation: *The Journal of Chemical Physics* **43**, 3237 (1965); doi: 10.1063/1.1697298

View online: <http://dx.doi.org/10.1063/1.1697298>

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R. W. GETZINGER AND G. L. SCHOTT

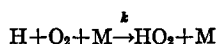
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(Received 25 June 1965)

Recombination in highly diluted, lean hydrogen-oxygen-argon mixtures with H_2/O_2 ratios of 0.50 and 0.33 has been investigated with a shock tube over the temperature range 1150°–1850°K for reaction pressures of 0.85–5.41 atm. An OH ultraviolet line absorption technique was used to follow the progress of the reaction after substantial equilibration of the rapid bimolecular reactions which form OH initially. It was determined that under these conditions the recombination process is third order and its rate, R_{reo} , obeys the empirical relationship

$$R_{\text{reo}} = k_{\text{eff}}[\text{H}][\text{O}_2][\text{Ar}].$$

k_{eff} was found to decrease slightly with increasing temperature and to depend to a small extent upon the composition of the reacting mixture. The experimental results indicate that the reaction



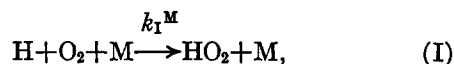
dominates the recombination process. Further analysis of the data made it possible to obtain from k_{eff} a value of $k(\text{M}=\text{Ar}) = 1.42 \times 10^{15} \text{ cc}^2/\text{mole}^2 \text{ sec}$ at 1500°K and an estimate of $k(\text{M}=\text{H}_2\text{O})/k(\text{M}=\text{Ar})$ of about 30. This value of $k(\text{M}=\text{Ar})$ has been combined with other experimental determinations to obtain the expression $k(\text{M}=\text{Ar}) = 8.6 \times 10^{14} \exp(1280 \pm 90/RT) \text{ cc}^2/\text{mole}^2 \text{ sec}$ which describes the data to within 20% over the entire temperature range from 225° to 1850°K.

INTRODUCTION

ALTHOUGH the chemical processes that bring about recombination in rich hydrogen-oxygen-diluent mixtures are by now quite well understood,¹⁻³ little information is available concerning the mechanism responsible for the corresponding decay of radicals in lean mixtures. This situation is to a large extent due to the fact that stable flames cannot be maintained for hydrogen/oxygen ratios of less than 1.0.⁴ Thus it has not been possible to bring the techniques of flame research to bear on this problem except at near-stoichiometric conditions. In addition, the large number of termolecular reactions that might be expected to contribute to the recombination process in lean mixtures have limited work in this regime by making the situation appear to be considerably more complex than in the presence of excess hydrogen.

However, some important information regarding the mechanism of recombination in mixtures with hydrogen/oxygen ratios between 0.5 and 2 is available from combustion studies at elevated temperatures. Thus evidence for the validity of the partial equilibrium approximation during recombination is available from measurements of the peak OH concentration following

the induction period in shock-wave experiments⁵ and from determinations of O and OH concentrations just before full equilibrium is attained in hydrogen-oxygen-diluent flames.⁴ Kaskan's flame experiments^{4,6} have also suggested that (1) recombination proceeds at a rate greater than can be accounted for by simple termolecular reactions involving H, OH, and O to form H_2 , H_2O , and O_2 , and (2) this rate is proportional to $[\text{OH}]^3$. In agreement with these results the recent flame study of Fenimore and Jones⁷ indicated that a substantial portion of recombination occurs by the reaction



where the general third-body M is in this case H_2O . An estimate of the rate constant $k_1^{\text{H}_2\text{O}}$ at 1350°K was thus obtained.⁷

The applicability of partial equilibrium to recombination in hydrogen-oxygen-diluent mixtures implies that the changes in chemical composition taking place during the approach to full equilibrium can be followed in detail by the measurement of a single pertinent quantity.⁸ An ultraviolet line absorption technique for observing the OH radical concentration in this chemical system at high temperature in a shock tube was

* This paper was presented before the Division of Physical Chemistry, American Chemical Society, 150th National Meeting, Atlantic City, New Jersey, September 1965.

¹ G. Dixon-Lewis, M. M. Sutton, and A. Williams, *Discussions Faraday Soc.* **33**, 205 (1962).

² J. L. J. Rosenfeld and T. M. Sugden, *Combust. Flame* **8**, 44 (1964).

³ G. L. Schott and P. F. Bird, *J. Chem. Phys.* **41**, 2869 (1964).

⁴ W. E. Kaskan, *Combust. Flame* **2**, 286 (1958).

⁵ G. L. Schott, *J. Chem. Phys.* **32**, 710 (1960).

⁶ C. P. Fenimore, *Chemistry in Premixed Flames* (Pergamon Press, Inc., New York, 1964), pp. 19–21.

⁷ C. P. Fenimore and G. W. Jones, *Symp. Combust.* **10th**, Cambridge, England, 1964, 489 (1965).

⁸ E. M. Bulewicz, C. G. James, and T. M. Sugden, *Proc. Roy. Soc. (London)* **A235**, 89 (1956).

TABLE I. Composition of experimental mixtures.

Designation	%H ₂	%O ₂	%Ar
A-1	1.00	2.00	97.00
A-2	1.00	3.00	96.00
A-3	2.75	5.50	91.75
A-4	1.44	2.87	95.69
A-5	0.97	1.94	97.09
A-6	0.73	1.47	97.80

developed in this laboratory a number of years ago⁹ and its recent application in a successful study of recombination in rich mixtures has been described.³ In the present work this technique has been employed to observe the decay of OH radicals in lean H₂-O₂-Ar mixtures over a wide range of compositions, temperatures, and densities. The result of this investigation has been the elucidation of several aspects of the mechanism of recombination in lean mixtures.

EXPERIMENTAL

The only feature of the present experimental design not described in Part IV³ was an improved method of making shock-velocity measurements. For this purpose the five platinum resistor gauges were replaced by an equal number of piezoelectric sensors.¹⁰ In addition to being more rugged, these devices gave output signals that were several orders of magnitude greater than the resistors, thus reducing considerably the amount of amplification required to fire the thyatrons and improving the uniformity of response of the gauges. This improved reliability made corrections for differences in circuitry response unnecessary. After amplification the gauge outputs were treated in the same manner as in Part IV.

The expansion section of the 10-cm-diam tube was lengthened to 522 cm for this work. The piezoelectric sensors were flush mounted at intervals of 80.00, 30.00, 30.00, and 29.94 cm along the tube beginning 348 cm from the diaphragm. The quartz windows through which the light beam used in measuring OH concentrations passed were located 1.3 cm downstream of the fourth gauge.

The six mixtures used in these experiments are listed in Table I. The compositions of these mixtures were established manometrically and mass spectrographic analysis of several of the batches confirmed the absence of all impurities but trace amounts of N₂ and CO₂. The expansion section of the shock tube was always filled with one of these mixtures to a pressure of 4–24 cm Hg and the driver section with H₂ to a pressure of 50–250 psia. In this manner reaction zone

temperatures of 1150°–1850°K and pressures of 0.85–5.14 atm were achieved. The lower temperature limit was imposed by the appearance of gas-dynamic instabilities, while at the lowest pressures insufficient recombination occurred during the period of observation to obtain reliable data. The upper pressure limit was the result of both the practical consideration of the strength of the shock tube and the theoretical expectation that at much higher pressures recombination would become so rapid that the partial equilibrium approximation would no longer be valid.

As with the rich mixtures in Part IV several experiments were repeated without the flash lamp energized to check emission between 3087.9 and 3098.1 Å from the heated reacting gases in the shock tube. It was confirmed that during the period over which recombination measurements were made emission was at least three orders of magnitude less than the radiation reaching the photomultiplier detector when the lamp was flashed. However, it should be noted that, in contrast to observations made in rich mixtures,³ at 1600°K in Mixture A-2 emitted radiation accounted for approximately 3% of that seen by the photomultiplier at the time when the OH concentration was rising to its peak, but decayed rapidly to a negligible amount thereafter. OH emission under similar conditions behind a shock front in a 5% H₂-95% air mixture was the subject of a recent investigation by Belles and Lauver.¹¹

As in Part IV the data obtained from these experiments consisted of photographs of (1) the raster trace showing the progress of the shock past the various gauge positions and (2) the absorption by OH of the incident radiation from the flash lamp as a function of time behind the shock front. In general the analysis of these data was carried out in a manner identical to that described in Part IV. Thus the technique for reducing the shock velocity data was unchanged. Similarly, Hugoniot computations for the initial conditions, shock velocities, and various extents of chemical reaction of interest in the present experiments were carried out for the same species and thermodynamic functions as before. Also unchanged was the basic method of determining the OH concentrations from the absorption data and average temperature (\bar{T}) and pressure (\bar{p}) of each experiment. However, in accordance with results suggested in the recent description of the calibration procedure for the OH line absorption technique,¹² slightly different values of the basic theoretical parameters were used. Thus in this work, the transition probability coefficient, F , was taken as 3.20×10^{-4} , the pressure broadening parameter, a , as $285\bar{p}$ (atm)/ T (°K), and the continuum background of the lamp as 3.47 units.

⁹ S. H. Bauer, G. L. Schott, and R. E. Duff, *J. Chem. Phys.* **28**, 1089 (1958).

¹⁰ Type LD-80M1 piezoelectric gauges manufactured by the Atlantic Research Corporation, Alexandria, Virginia.

¹¹ F. E. Belles and M. R. Lauver, *J. Chem. Phys.* **40**, 415 (1964).

¹² P. F. Bird and G. L. Schott, *J. Quant. Spectry. Radiative Transfer* (to be published).

RECOMBINATION KINETICS

The main result of the complete reduction of the data is a curve of $[\text{OH}]$, the concentration of OH in moles per cubic centimeter, versus time for each experimental shock. It is desired to use these data to acquire information about the chemical reactions that contribute significantly to recombination under the experimental conditions. It has been the practice in past high-temperature studies of recombination in either rich or lean hydrogen-oxygen-diluent mixtures in which $[\text{OH}]$ or $[\text{H}]$ was the observable to accomplish this result by relating $d[\text{OH}]/dt$, or $d[\text{H}]/dt$, directly to the rate of decrease in the total number of chemical species present in the system.^{1-4,8,13} This approach has been successful because of certain simplifications that were valid for the particular experimental conditions being employed.

To appreciate these simplifications, let us examine them in terms of the stoichiometric and partial equilibrium relationships that bring them about, first in rich mixtures and then in lean. In rich mixtures, an appropriate stoichiometric expression for R_{rec} , the sum of the net forward rates of all recombination reactions, is¹⁴

$$R_{\text{rec}} = -\frac{1}{2} \left\{ \left(\frac{\partial}{\partial t} \right) ([\text{H}] + [\text{OH}] + 2[\text{O}] + 2[\text{O}_2]) \right\}_p, \quad (1)$$

where partial derivatives of concentrations with respect to time at fixed density and elemental composition of the system are indicated on the right-hand side.

The partial equilibrium relationships affecting the four species whose derivatives appear are such that: (1) the principal stoichiometric result of recombination is $2\text{H} \rightarrow \text{H}_2$, so that $(\partial[\text{H}]/\partial t)_p$ dominates the expression throughout the reaction, and (2) the relationship between $[\text{OH}]$ and $[\text{H}]$ is a particularly simple one,

$$[\text{OH}] = (K_3[\text{H}_2\text{O}]/[\text{H}_2])[\text{H}], \quad (2)$$

where K_3 is the equilibrium constant for the reaction



These relationships applied to the recombination reaction in rich post-flame gases or dilute rich mixtures in shock waves, where temperature, density, $[\text{H}_2]$, and $[\text{H}_2\text{O}]$ do not change dramatically, yield approximate proportionality between $-d[\text{OH}]/dt$ and R_{rec} . They also yield convenient expressions of the rates of the recombination reactions between two H atoms and between H and OH in terms of either $[\text{H}]^2$ or $[\text{OH}]^2$.

The stoichiometric expression analogous to Eq. (1) that is applicable in lean mixtures is¹⁴

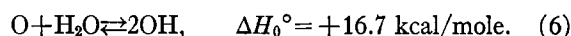
$$R_{\text{rec}} = -\frac{1}{4} \left\{ \left(\frac{\partial}{\partial t} \right) ([\text{OH}] + 2[\text{O}] + 2[\text{H}_2] + 3[\text{H}]) \right\}_p, \quad (4)$$

in terms of species which are consumed, more or less quantitatively, during recombination. The key to the

stoichiometric complexity of recombination in lean mixtures is provided by the partial equilibrium relationship between $[\text{OH}]$ and $[\text{O}]$,

$$[\text{OH}]^2 = K_6[\text{H}_2\text{O}][\text{O}], \quad (5)$$

where K_6 is the equilibrium constant for the reaction



Because of the quadratic relationship given by Eq. (5) under conditions of nearly constant $[\text{H}_2\text{O}]$, neither $[\text{OH}]$ nor $[\text{O}]$ is dominant throughout the course of recombination. Moreover, H and H_2 are energetically favored in the partial equilibrium relationships, and their rates of disappearance are appreciable also, particularly at lower temperatures. Thus even if one were to reduce $[\text{H}]$ and $[\text{H}_2]$ to negligible levels by the use of a large excess of O_2 , Eq. (5) is unaffected, and there is no simple relationship between $(\partial[\text{OH}]/\partial t)_p$ and the right-hand side of Eq. (4) except very near complete equilibrium,^{4,6} where

$$R_{\text{rec}} \sim -\frac{1}{4} (d[\text{OH}]/dt). \quad (7)$$

None of these considerations, of course, were appropriate to the lean flame study of Fenimore and Jones,⁷ who determined the $[\text{H}]$ and temperature profiles under conditions where the density was not constant and the partial equilibrium approximation was probably not valid.

Although the present experiments with shock waves were carried out under conditions where the approximations of partial equilibrium and constant density were quite satisfactory, it was not possible to observe a sufficient amount of recombination to reach the regime of validity of Eq. (7). Since the more general equation resulting from (4) and (5) was observed to be sufficiently complex that much of the physical meaning was lost in the mathematics, it was decided to develop an expression in terms of the more fundamental quantity ν , a nondimensional progress variable defined as

$$\nu = (N - N_{\text{eq}})/(1 - N_{\text{eq}}). \quad (8)$$

In Eq. (8) N is the mole number ratio, i.e., total moles per initial mole, at any point during recombination, and N_{eq} is the value of this quantity at full equilibrium. Thus ν is equal to 1 in the absence of any dissociation or recombination and 0 when complete equilibrium has been reached. It should be noted that partial equilibrium plus the value of ν completes the specification of the system. Thus it is an appropriate fundamental parameter to use to follow recombination between the hypothetical partial equilibrium state $\nu=1$ and the ultimate full equilibrium state $\nu=0$.

Before explaining how values of ν were obtained from the experimental quantity $[\text{OH}]$ we derive an expression analogous to Eq. (4) in terms of ν . Let us first define the quantity N_i , the number of moles of the i th species

¹³ W. E. Kaskan, *Combust. Flame* **2**, 229 (1958).

¹⁴ W. E. Kaskan and G. L. Schott, *Combust. Flame* **6**, 73 (1962).

per initial mole of gas mixture, or mole number ratio of species i , by the expression

$$\rho(N_i/M_0) = [I], \quad (9)$$

where M_0 is the mean molecular weight in the initial gas mixture. Since R_{reo} is defined as the total rate of consumption of all m species in the system by chemical change, or

$$-\sum_{i=1}^m \left(\frac{\partial [I]}{\partial t} \right)_p,$$

it follows that

$$-R_{\text{reo}} = \frac{\rho}{M_0} \sum_{i=1}^m \frac{dN_i}{dt} = \frac{\rho}{M_0} \frac{dN}{dt}, \quad (10)$$

with

$$N = \sum_{i=1}^m N_i.$$

From the definition of ν and the fact that $dN/dt = (d/dt)(N - N_{\text{eq}})$ it is possible to write

$$-R_{\text{reo}} = (\rho/M_0)(1 - N_{\text{eq}})(d\nu/dt), \quad (11)$$

which is the desired expression. For shock experiments, however, it is convenient to introduce the relationship between molecule time, t , and laboratory time, τ . For shock waves in a gas mixture which is initially at rest with respect to the experimental apparatus (incident shock waves) this expression is

$$dt = (\rho/\rho_0)d\tau, \quad (12)$$

where ρ_0 is the density of the unshocked gas. Combining Eqs. (11) and (12) with the ideal gas law results in

$$-R_{\text{reo}} = (p_0/RT_0)(1 - N_{\text{eq}})(d\nu/d\tau), \quad (13)$$

with p_0 and T_0 being the pressure and temperature of the unshocked gas. Since for a given experiment p_0 , T_0 , and $(1 - N_{\text{eq}})$ are constant Eq. (13) enables us to use $d\nu/d\tau$ directly to investigate R_{reo} . It should be noted that in lean mixtures $d\nu/d\tau$ is proportional to $d[\text{OH}]/d\tau$ if Eq. (7) is valid.

To make use of Eq. (13) it was found that the experimentally determined $[\text{OH}]$ vs τ curve had to be treated by a further analysis procedure to accomplish the following: (1) to obtain for each OH concentration the corresponding value of ν and the complete composition of the system, and (2) to obtain the slope $d\nu/d\tau$ at any observed value of ν during recombination.

The first objective was achieved by preparing a table for each experiment showing the concentration of the species H_2 , O_2 , H_2O , OH , H , and O present at partial equilibrium for each of a carefully selected series of ν values covering the range $0 \leq \nu \leq 1$, and interpolating for each experimentally determined $[\text{OH}]$. Thus for each $[\text{OH}]$ six interpolations were performed. These were carried out by a special computer code that used

ν and the natural logarithms of the concentrations as variables. Cubic equations were fit to four appropriate sets of points, two of whose values of $[\text{OH}]$ fell on each side of the observed $[\text{OH}]$, except near the extremes of the table. In the rare instances where one or more experimental $[\text{OH}]$ was greater than $[\text{OH}]_{\nu=1.0}$ the results of these particular interpolations were ignored. The concentration of argon was found to be so nearly constant over the recombination zone that its interpolation could readily be carried out by hand.

The accuracy of this procedure was easily checked by making Hugoniot computations with selected ν values obtained by interpolation. Computed concentrations of the various species were then compared with the interpolated results. Excellent agreement was obtained between the two sets of concentrations for a variety of cases. Thus it is felt that the accuracy of this interpolation technique has been quite satisfactorily verified.

Obtaining the slopes $d\nu/d\tau$ from the data relating ν and τ , however, proved to be considerably more difficult. This problem arose because in most of the recombination experiments an initial very rapid decrease in ν was followed by a considerably more gradual decay which extended over much of the observation period. Fitting this behavior with a satisfactory analytical expression necessitated some trial-and-error searching. A quadratic expression of $\ln \nu$ in terms of $\ln \tau$ was eventually found to reproduce the data satisfactorily and provided the desired slopes for any value of ν . A period of recombination of some 400–500 μsec was usually all that was fit in this manner, since changes in ν beyond this point were generally quite small. Confidence in the reliability of the computed $d\nu/d\tau$ is provided in two ways: (a) by agreement with a number of slopes taken by eye from large linear plots of ν vs τ and (b) by the consistency and lack of scatter in the results, particularly those dealing with the large, direct effect of total pressure on the rate of recombination.

At this point it will be instructive to examine how the relative concentrations of the various species behave as a function of ν during the course of a typical recombination experiment. The calculated partial equilibrium variation of the mole fractions of each of the six reactive species is shown in Fig. 1 for a typical shock in Mixture A-2 at approximately 1500°K. It should be noted that only the shock velocity and initial experimental conditions are required for the computation of these curves. As the appearance of this figure would not be essentially altered for any of the experimental conditions encountered in this work, a few observations of general applicability are appropriate:

(a) Initially as O_2 and H_2O are formed the mole fractions, or concentrations, of O , H , and H_2 decrease much more rapidly than OH , eventually reaching a very much lower concentration as full equilibrium is approached.

(b) Due to contributions from the other terms in Eq. (4) OH does not become a sensitive measure of ν until $\nu \leq 0.20$. However, it should be noted that in the region $0.20 \geq \nu \geq 0.01$ [OH] is still at a level that can be conveniently observed experimentally. Thus it is in this region that our experimental technique can best be used to follow ν .

(c) The concentrations of H_2O and O_2 , and, of course, Ar are nearly constant over the entire range $1 \geq \nu \geq 0$. In addition, in the region of interest, $0.20 \geq \nu \geq 0.01$, $[\text{O}_2]$ is more than a factor of 10 greater than the concentrations of the three radicals and H_2 .

(d) At $\nu < 0.01$ $[\text{OH}] \gg [\text{H}]$, $[\text{O}]$, and $[\text{H}_2]$, and Eq. (7) becomes valid. These are the conditions under which Kaskan's flame experiments⁴ were carried out.

It should be noted that of the approximately 500 μsec of reaction time available for observation behind the shock front generally only some 50 μsec are required to attain a ν value of 0.20. Most of the remaining time was consumed in the regime from $\nu = 0.20$ to $\nu = 0.01$.

At this point let us return to Eq. (13) and apply the information from Fig. 1, as well as some experimental results to our investigation of the reactions that contribute significantly to R_{rec} . If l termolecular reactions account for the observed recombination rate then

$$R_{\text{rec}} = \sum_{j=1}^l k_j M_j [A_j][B_j][C_j], \quad (14)$$

where $[A_j]$ and $[B_j]$ are the concentrations of the two reactive species involved in reaction j , $k_j M_j$ is the specific rate constant of the j th reaction for the particular third body M_j , and $[C_j]$ represents the weighted sum of concentrations of all the species in the system acting as third bodies in Recombination Reaction j .

$$[C_j] = \sum_{i=1}^m a_{ji} [I], \quad (15)$$

where $a_{ji} = k_j^I / k_j^{M_j}$ is the efficiency of species I relative to M_j in promoting Reaction j . In general, of course, M_j can be any of the species present in the system and can be different for any of the j reactions. However, in future treatment of the heavily diluted mixtures used in this work M_j is Ar for all j reactions.

For ideal gases

$$R_{\text{rec}} = \left(\frac{p}{RT} \right)^3 \sum_{j=1}^l k_j^{\text{Ar}} [x_{A_j}] [x_{B_j}] \sum_{i=1}^m a_{ji} [x_I], \quad (16)$$

where the x 's represent mole fractions and $p = \pi p_0$ with π representing the dimensionless pressure ratio across the shock wave.

Equations (13) and (16) relate $d\nu/d\tau$ to pressure for all conditions having the same values of temperature and the mole fractions. This relationship can be tested by comparing values of $d\nu/d\tau$ obtained at common values of ν in experiments covering a range of p_0 . The

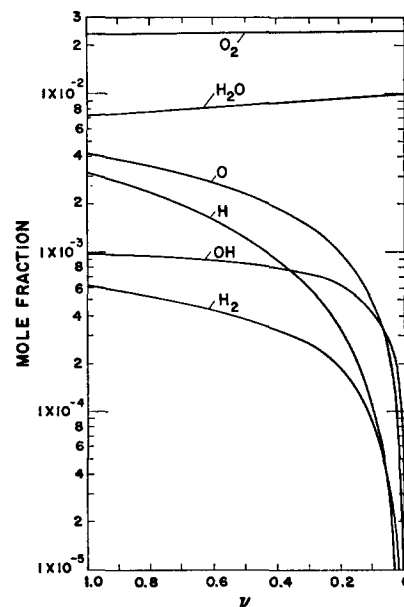


FIG. 1. Dependence of mole fractions upon ν for recombination under partial equilibrium conditions. Mixture: A-2; $p_0 = 12.01$ cm Hg; and shock velocity = 1.1740 mm/ μsec . $T(\text{no reaction}) = 1458^\circ\text{K}$, $T(\nu = 1.0) = 1459^\circ\text{K}$, $T(\nu = 0.0) = 1550^\circ\text{K}$, and $\bar{T} = 1504^\circ\text{K}$.

same temperatures, pressure ratios, and mole fractions are obtained when a given initial mixture is shocked at a given shock velocity. This is because the partial equilibrium relationships are independent of pressure and under these experimental conditions the hydrogen is completely converted to water at full equilibrium so that varying the initial pressure has a negligible effect on N_{eq} and the recombination path is reproduced identically.

The relationship to be tested takes the form

$$-\frac{d\nu}{d\tau} = p_0^2 \left(\frac{\pi}{T} \right)^3 \frac{T_0}{R^2(1 - N_{\text{eq}})} \times \sum_{j=1}^l k_j^{\text{Ar}} [x_{A_j}] [x_{B_j}] \sum_{i=1}^m a_{ji} [x_I]. \quad (17)$$

Thus, for such experiments $-d\nu/d\tau$ should be proportional to p_0^2 and a plot of $\ln[-d\nu/d\tau]$ vs $\ln p_0$ at any value of ν should be a straight line of slope = 2.

Of course it is impossible to reproduce any given shock velocity at will. Nevertheless, experimental shocks with nearly the desired velocity can be repeated as often as desired and differences in the values of $d\nu/d\tau$ at any ν value can be compared. In this manner it was determined that the recombination process, as indicated by values of $d\nu/d\tau$, was not very sensitive to small variations in the shock velocity.

Experiments in which p_0 was varied, but the initial composition and shock velocity were held constant, were carried out in both Mixtures A-1 and A-2 at $\bar{T} \sim 1480^\circ\text{K}$. The results of work with A-2 at $\nu = 0.10$ over a fourfold

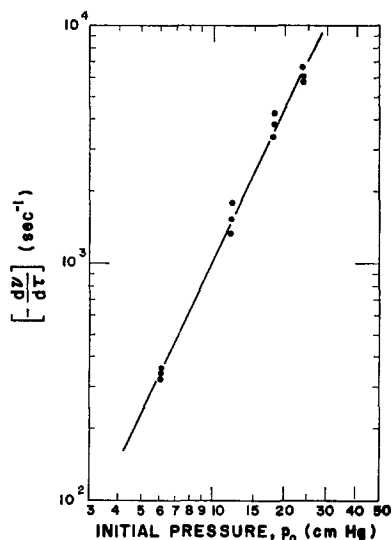


FIG. 2. Effect of total pressure upon recombination rate. Mixture: A-2; $\nu=0.10$; and $T \sim 1480^\circ\text{K}$. Slope of line determined by least-squares fit $= 2.12 \pm 0.06$.

range of p_0 are shown in Fig. 2. A least-squares fit through these points yielded a slope of 2.12 ± 0.06 . Similarly, for A-1 at $\nu=0.10$ for initial pressures of 10, 15, and 20 cm Hg, a least-squares fit through 8 points produced an exponent of 1.88 ± 0.10 . Similar slopes were obtained for fits at $\nu=0.05$ and 0.15 in both cases. It should be noted that in Mixture A-1 at $p_0=5$ cm Hg an insufficient amount of recombination was seen during the observation period for the desired ν values to be attained. These results establish the fact that recombination is brought about by three-body processes, which is consistent with its separation from the region of rapid bimolecular reactions that follows immediately behind the shock front.

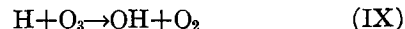
In order to develop Eq. (14) further at this point it is necessary to consider what recombination reactions might make significant contributions to R_{rec} under these conditions. For this purpose we refer again to the regime $0.20 \geq \nu \geq 0.01$ in Fig. 1. In lean mixtures, as opposed to fuel-rich mixtures, a reaction path with one of the stable species present in large concentration, i.e., O_2 , is possible during recombination. Thus it might be expected that if the reaction rate constant of either (I) or



was not very small these two processes would make up a large amount of R_{rec} in our experiments. However, it is possible that under these conditions recombination of two radicals may dominate, or at least strongly influence, R_{rec} and such processes must be considered also.

In Table II are listed all termolecular reactions that might reasonably be expected to contribute significantly to R_{rec} . The species HO_2 , O_3 , and H_2O_2 , if produced by (I), (II), (III), and (VII), would disappear imme-

diately as the result of fast bimolecular steps such as those discussed by Fenimore and Jones for HO_2^7 or



Thus the concentration of these species would be maintained at a negligibly small level.

In attempting to distinguish between the reactions in Table II it was found useful to classify them according to their order with respect to $[\text{OH}]$, the observable, and with respect to $[\text{H}]$. This can easily be done in an approximate way by making use of partial equilibrium relationships such as (6) for constant $[\text{O}_2]$ and $[\text{H}_2\text{O}]$. Thus from the results that $[\text{H}] \propto [\text{OH}]^3$ and $[\text{O}] \propto [\text{OH}]^2$ the two right-hand columns in Table II were derived.

Before discussing the experimental investigation of reaction order it will be informative to make an estimate of the relative importance in our experiments of the reactions listed in Table II. The rate constants of (VI)¹⁵ and (VIII)³ are known, and in the regime of interest—see Fig. 1—their contributions to the observed recombination rate should be negligible. Similarly it is possible to rule out (VII) by combining the rate constant for the dissociation of H_2O_2 for $\text{M}=\text{H}_2\text{O}_2$ ¹⁶ with K_{VII}^{17} and a reasonable estimate of the relative efficiency of argon to show that $k_{\text{VII}}^{\text{Ar}}$ is small. k_{V}^{M} is known to be $\sim 10k_{\text{VIII}}^{\text{M}}$ at these temperatures,³ while practically nothing is known about k_{IV}^{M} ¹⁸ or $k_{\text{III}}^{\text{M}}$. Thus if the rate constants of (I) and (II) should be small it is possible that one or more of these three reactions might increase R_{rec} significantly.

Another factor to consider, however, is the low dissociation energy of O_3 [$D_0^\circ(\text{O}-\text{O}_2) = 24.2$ kcal/mole].¹⁷

TABLE II. Recombination reactions and their order with respect to $[\text{OH}]$ and $[\text{H}]$.^a

Designation	Reaction	x	y
I	$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	3	1
II	$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$	2	2/3
III	$\text{O} + \text{OH} + \text{M} \rightarrow \text{HO}_2 + \text{M}$	3	1
IV	$\text{H} + \text{O} + \text{M} \rightarrow \text{OH} + \text{M}$	5	5/3
V	$\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$	4	4/3
VI	$\text{O} + \text{O} + \text{M} \rightarrow \text{O}_2 + \text{M}$	4	4/3
VII	$\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$	2	2/3
VIII	$\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$	6	2

^a x and y are defined by the relations: Rate of reaction $i \propto [\text{OH}]^x$ or $[\text{H}]^y$.

¹⁵ J. H. Kiefer and R. W. Lutz, *J. Chem. Phys.* **42**, 1709 (1965).

¹⁶ D. E. Hoare, J. B. Protheroe, and A. D. Walsh, *Trans. Faraday Soc.* **55**, 548 (1959).

¹⁷ *JANAF Interim Thermochemical Tables* (The Dow Chemical Company, Midland, Michigan, 1960), and supplements through March 1964.

¹⁸ P. Hartek and R. R. Reeves, *Chemical Reactions in the Lower and Upper Atmosphere* (Interscience Publishers, Inc., New York, 1961), Chap. 14, p. 237.

Hand calculations comparing the dissociation rate of O_3 ¹⁹ with the bimolecular collision frequency of (IX) near 1500°K indicate that under our experimental conditions the net forward rate of (II) ($=R_{II}^{for}-R_{II}^{rev}$) is considerably less than R_{II}^{for} . Since $D_0^\circ(H-O_2)$ is much larger ($=45.9$ kcal/mole)¹⁷ this behavior would not be expected from HO_2 until much higher temperatures. In view of the values of k_I^M obtained at lower temperatures^{20,21} and the fact that the $[H][O_2]$ product is at least as large as the radical-radical products for Reactions (III)–(VIII) in Table II, it would not be surprising at all to find that Reaction (I) dominates R_{reo} .

With these observations in mind the experimental results can be compared with Eqs. (13) and (14) to obtain a better understanding of the recombination process. As a first step plots of $\ln[-dv/d\tau]$ vs $\ln[OH]$ were prepared for a number of experiments to obtain slopes for comparison with Table II. A reaction order of approximately three was consistently obtained from these curves suggesting important contributions from Reactions (I) and (III). The same data were plotted

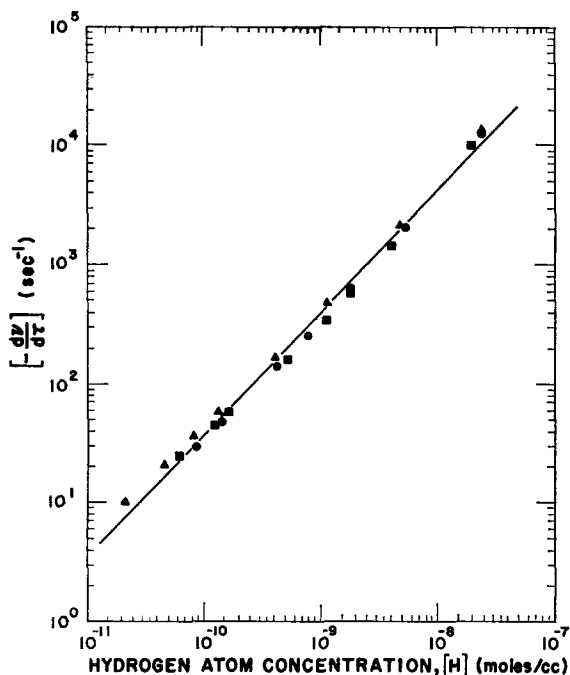


FIG. 3. Dependence of recombination rate on hydrogen atom concentration for mixture A-1. Results of three experiments with $p_0=15$ cm Hg and $\bar{T}\sim 1530^\circ\text{K}$ are noted by symbols \bullet , \blacksquare , and \blacktriangle ; ν values are between 0.37 and 0.005 and cover a period of about 600 μsec . Slope of line determined by least-squares fit $=1.03\pm 0.02$.

¹⁹ W. M. Jones and N. Davidson, J. Am. Chem. Soc. **84**, 2868 (1962).

²⁰ M. A. A. Clyne and B. A. Thrush, Proc. Roy. Soc. (London) **A275**, 559 (1963).

²¹ R. R. Baldwin, Symp. Combust. 9th Ithaca, New York, 1962, 218 (1963).

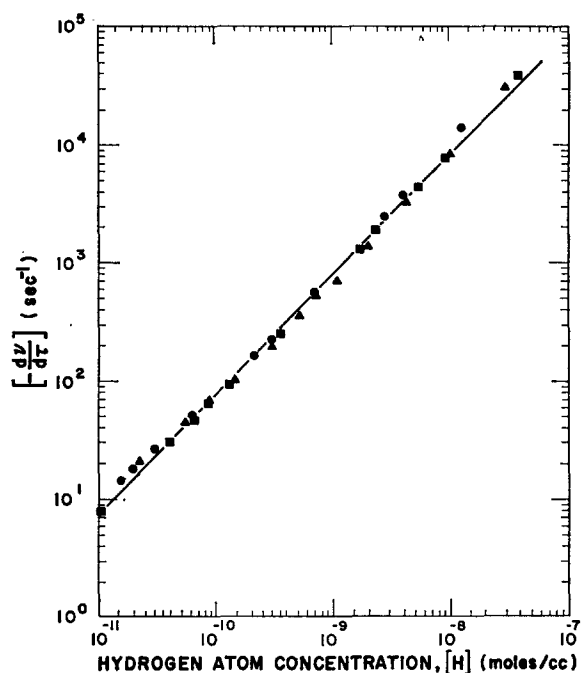


FIG. 4. Dependence of recombination rate on hydrogen atom concentration for mixture A-2. Results of three experiments with $p_0=15$ cm Hg and $\bar{T}\sim 1415^\circ\text{K}$ are denoted by symbols \bullet , \blacksquare , and \blacktriangle ; ν values are between 0.55 and 0.004 and cover a period of about 450 μsec . Slope of line determined by least-squares fit $=1.01\pm 0.01$.

as $\ln[-dv/d\tau]$ vs $\ln[H]$ to enable a clearer differentiation between the various reaction orders. Figures 3 and 4 represent such plots for Mixtures A-1 and A-2, respectively, for different groups of experiments carried out with nearly identical initial conditions and shock velocities. In Fig. 3, $\bar{T}\sim 1530^\circ\text{K}$ and $p_0=15$ cm Hg, while in Fig. 4, $\bar{T}\sim 1415^\circ\text{K}$ and $p_0=15$ cm Hg. Least-squares fits gave slopes of 1.03 ± 0.02 and 1.01 ± 0.01 , respectively, for the best straight lines through the data.

Thus, a clear first-order dependence has been observed over a three to four orders of magnitude change in $[H]$. This general result was found to be approximately true for all experiments but those few carried out at the highest temperatures ($T>1750^\circ\text{K}$) where slopes ~ 1.10 were observed on plots of this type. This point is considered later in this paper.

In view of these results and the considerations presented above it appears appropriate to specialize Eq. (14) to Reactions (I) and (III) in order to examine the dependence of the recombination rate upon the initial composition of the reaction mixture. For these reactions, Eqs. (13) and (14) become

$$(p_0/RT_0)(1-N_{eq})(dv/d\tau) = -k_{eff}[H][O_2][Ar]. \quad (18)$$

The effective rate coefficient, k_{eff} , is given by

$$k_{eff} = k_I \frac{[C_I]}{[Ar]} + K_{20} k_{III} \frac{[C_{III}]}{[Ar]}, \quad (19)$$

TABLE III. Summary of experimental results.*

\bar{T} (calc)	p_0 (obs)	$\nu \times 10^2$ (calc)	k_{eff} $\times 10^{-15}$	$[\text{H}_2\text{O}]/[\text{Ar}]$ $\times 10^2$	k_1^{Ar} $\times 10^{-15}$	\bar{T} (calc)	p_0 (obs)	$\nu \times 10^2$ (calc)	k_{eff} $\times 10^{-15}$	$[\text{H}_2\text{O}]/[\text{Ar}]$ $\times 10^2$	k_1^{Ar} $\times 10^{-15}$
Mixture A-1:						Mixture A-2: (Continued)					
1164	15.02	5.7	1.94	1.01	1.49	1252	15.00	4.0	2.33	1.03	1.78
1176	14.98	3.8	2.19	1.02	1.68	1313	15.01	5.4	2.26	1.02	1.73
1178	14.99	5.5	2.30	1.01	1.77	1317	15.02	3.8	2.52	1.01	1.93
1198	15.00	5.3	2.41	1.01	1.85	1344	15.02	5.7	2.19	1.02	1.68
1204	15.02	3.6	2.14	1.01	1.64	1406	15.01	7.0	1.97	1.01	1.51
1214	14.99	4.3	1.87	1.01	1.44	1408	15.01	7.8	2.17	1.01	1.67
1234	15.01	3.6	2.25	1.02	1.72	1411	6.01	8.2	1.64	1.01	1.26
1272	15.00	2.4	2.48	1.00	1.91	1430	15.00	3.7	2.39	1.00	1.84
1272	14.99	2.7	1.93	1.02	1.48	1449	11.99	6.0	2.24	1.01	1.72
1276	15.01	3.3	1.88	1.02	1.44	1459	6.01	8.3	1.94	1.01	1.49
1306	15.00	3.3	2.12	1.02	1.62	1459	18.01	3.4	1.91	1.02	1.46
1308	15.01	6.8	1.95	1.00	1.50	1460	18.00	3.3	2.32	1.01	1.78
1345	14.99	3.6	1.95	1.01	1.50	1470	6.00	9.0	1.85	1.01	1.42
1378	15.02	3.2	1.73	1.01	1.33	1486	18.01	6.2	1.96	1.01	1.50
1380	15.00	3.2	1.89	1.01	1.45	1494	12.01	6.0	1.68	1.01	1.29
1386	15.01	4.9	2.04	1.01	1.57	1504	12.01	5.8	2.05	1.01	1.57
1394	15.01	3.0	1.65	1.02	1.26	1506	24.00	3.7	1.90	1.02	1.45
1428	15.00	4.0	1.55	1.01	1.19	1512	24.01	5.0	2.31	1.02	1.77
1430	14.99	4.7	2.18	1.01	1.67	1522	24.00	4.8	1.99	1.02	1.52
1432	15.01	8.5	1.79	1.00	1.38	1594	15.02	4.0	2.08	1.00	1.60
1440	9.99	6.1	1.87	0.994	1.44	1609	15.02	5.4	1.83	1.01	1.40
1448	14.99	4.8	2.22	1.01	1.70	1648	14.99	5.2	1.96	1.01	1.50
1452	10.01	6.9	1.96	1.00	1.51	Mixture A-3:					
1480	15.02	6.7	1.62	1.00	1.25	1596	5.45	6.1	2.75	2.90	1.47
1483	14.91	6.0	1.67	1.00	1.28	1600	5.44	5.2	2.64	2.84	1.43
1486	14.99	5.1	1.88	1.01	1.44	1626	5.46	6.1	2.48	2.89	1.33
1489	19.98	4.1	1.86	1.01	1.43	1792	5.46	5.7	2.18	2.88	1.17
1496	10.00	6.2	2.45	1.00	1.88	1800	5.45	8.8	2.26	2.85	1.22
1506	15.01	4.4	1.46	1.01	1.12	Mixture A-4:					
1517	20.05	4.2	1.68	1.01	1.29	1562	10.44	4.9	2.28	1.47	1.58
1518	15.01	2.1	1.68	1.02	1.29	1564	10.44	6.5	1.64	1.46	1.14
1520	19.99	3.6	1.79	1.01	1.37	1576	10.44	5.4	1.99	1.46	1.38
1538	15.01	6.2	1.60	1.00	1.23	1724	10.46	4.5	1.52	1.44	1.06
1542	14.99	4.7	1.89	1.01	1.45	1737	10.45	4.5	1.70	1.46	1.18
1572	12.01	7.4	1.20	1.00	0.923	1740	10.45	4.0	2.13	1.44	1.49
1614	12.01	6.5	1.12	1.00	0.862	Mixture A-5:					
1638	12.03	5.3	1.61	1.00	1.24	1532	15.44	3.1	2.15	0.984	1.66
1638	16.01	4.3	1.75	1.01	1.34	1559	15.45	3.0	1.67	0.984	1.29
1641	7.99	12.8	1.32	0.992	1.02	1576	15.44	4.4	1.70	0.972	1.32
1656	16.01	3.9	1.83	1.01	1.40	1700	15.44	4.3	1.97	0.973	1.52
1660	16.00	3.7	1.78	1.01	1.37	1708	15.47	4.5	1.42	0.973	1.10
1686	14.83	3.9	1.51	1.01	1.16	1727	15.43	2.7	2.06	0.980	1.59
1696	15.01	8.8	1.60	0.988	1.23	Mixture A-6:					
1710	14.98	7.9	1.78	0.988	1.37	1550	20.45	2.7	1.68	0.735	1.38
1712	14.99	5.4	2.53	1.00	1.95	1556	20.45	3.8	1.50	0.732	1.23
1731	16.01	3.1	1.22	1.01	0.936	1582	20.47	2.4	1.51	0.733	1.24
1734	15.99	6.6	1.31	0.992	1.01	1657	20.44	3.1	1.44	0.729	1.18
1818	15.00	7.6	1.50	0.988	1.16	1673	20.47	3.9	1.14	0.733	0.935
1824	15.01	4.6	1.31	1.00	1.01						
1849	15.00	4.7	1.40	1.00	1.08						
Mixture A-2:											
1167	15.01	2.8	2.04	1.03	1.56						
1224	15.02	7.7	2.07	1.02	1.59						

* Temperatures are in degrees Kelvin, pressures in centimeters of mercury, and k_{eff} and k_1^{Ar} in (centimeters³)/mole² seconds.

which embodies K_{20} , the equilibrium constant of the partial equilibrium reaction



between the reactants of recombination Reactions (I) and (III).

Table III lists values of k_{eff} computed from Eq. (18) for 96 experimental runs at $0.02 < \nu < 0.13$. These re-

sults cover a temperature range of 1150°–1850°K, as can be seen from the mean reaction temperatures in Column 1. Column 2 lists the initial pressure of each experiment. Column 3 shows the value of ν at which the quantity k_{eff} in the fourth column was derived. The proportionality between $d\nu/dr$ and the first power of $[\text{H}]$ demonstrated in Figs. 3 and 4 assures that k_{eff} is not dependent upon the precise value of ν at which

it is evaluated in a particular experiment, since $[O_2]$ and the other major third-body concentrations are all substantially constant throughout each experiment. Nevertheless, the constancy of k_{eff} was verified at other points in the course of the experiments, to further justify the summarization of the results by single values of dv/dr and k_{eff} .

An important result contained in Table III is that there is no significant difference between the values of k_{eff} observed in Mixtures A-1 and A-2. Between these two mixtures, the initial O_2 mole fraction was varied between 0.02 and 0.03, yielding O_2 concentrations differing by a factor of 5/3 in the reaction products, and very little difference in the mole fractions of the other significant constituents in the reacting mixture. Thus the correctness of the factor $[O_2]$ in the rate expression is demonstrated over the range of temperature of these results.

It is also apparent from Table III that the values of k_{eff} in both Mixtures A-1 and A-2 are of a reasonable magnitude for a three body rate coefficient, and that they decrease slightly with increasing temperature, as many three-body rate coefficients do. This small decrease in k_{eff} between 1150°K and 1850°K can be used to assess the relative importance of Reactions (I) and (III) in the recombination mechanism, something that cannot be done by varying concentrations at a particular temperature because of the partial equilibrium relationship, Eq. (20). The values of K_{20} computed from thermodynamic data¹⁷ near the extremes of the experimental temperature range are 0.009 at 1100°K and 0.154 at 1800°K. This seventeenfold increase in K_{20} accompanying a decrease in k_{eff} indicates that the k_{III} term in Eq. (19) is unimportant over most, if not all, of the temperature range of our experiments, and is entirely negligible at the lower temperatures. Accordingly we proceed to ignore it, and to pursue the dependence of k_{eff} upon mixture composition as being that of the k_I term, understanding that the resulting values of k_I^M embody a small, quantitatively uncertain contribution from the kinetically indistinguishable Reaction (III).

It is evident from the results in Table III that Mixtures A-3 through A-6 demonstrate a systematic decrease in k_{eff} with greater dilution of the H_2+2O_2 reactive mixture in the inert carrier. We proceed, therefore, to treat this variation of k_{eff} as a variation in the third-body factor, $[C_I]$, in Eq. (19). At the ν values considered in this work, the mole fractions of H, H_2 , O, and OH are at least a factor of 10^3 smaller than that of Ar, as is illustrated in Fig. 1. In view of the relative efficiencies determined for a large number of molecules as third bodies in Reaction (I) from second explosion limit measurements, we feel justified in neglecting specific contributions from these species in the formulation of $[C_I]$, and in treating the O_2 contribution as of secondary importance to H_2O . Accordingly, we retain the Ar, H_2O , and O_2 terms, and formulate the third

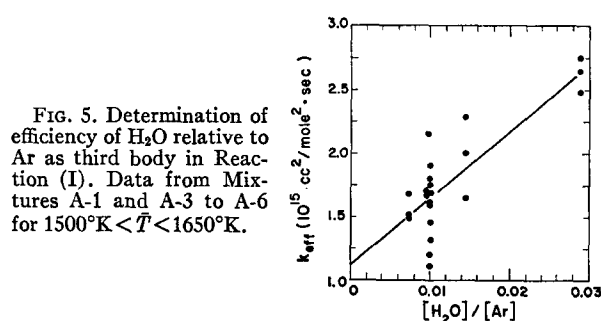


FIG. 5. Determination of efficiency of H_2O relative to Ar as third body in Reaction (I). Data from Mixtures A-1 and A-3 to A-6 for $1500^\circ K < T < 1650^\circ K$.

body effect upon k_{eff} as

$$k_{eff} = k_I^{Ar} \left\{ 1 + a_{I,H_2O} \frac{[H_2O]}{[Ar]} \left(1 + \frac{a_{I,O_2}}{a_{I,H_2O}} \frac{[O_2]}{[H_2O]} \right) \right\} \\ = k_I^{Ar} \{ 1 + \alpha ([H_2O]/[Ar]) \}. \quad (21)$$

α is equal to $(a_{I,H_2O} + 1.5a_{I,O_2})$ for all mixtures except A-2, for which it has the value $(a_{I,H_2O} + 2.5a_{I,O_2})$. Figure 5 shows a plot of k_{eff} vs $[H_2O]/[Ar]$ for all those data in Table III for mixtures A-1 and A-3 through A-6 in the temperature range 1500°–1650°K. A least-squares fit to these points yielded an intercept, $k_I^{Ar} = 1.12 \pm 0.11 \times 10^{15} \text{ cc}^2/\text{mole}^2 \text{ sec}$ and a value for α of 47 ± 7 . A similar treatment of the data for these mixtures between 1650° and 1800°K yielded $k_I^{Ar} = 1.29 \pm 0.12 \times 10^{15} \text{ cc}^2/\text{mole}^2 \text{ sec}$ and $\alpha = 26 \pm 10$.

As has been stated above, it is not possible from our data to discern any effect of the greater mole fraction of O_2 in Mixture A-2 upon the value of k_{eff} . This is not surprising if Eq. (18) is correct, for although O_2 is present in significant concentrations in the reacting mixtures and therefore should contribute to α , it would not be possible within the range of the present experiments to distinguish such an effect from the order of the recombination reaction with respect to O_2 since the ratio $a_{I,O_2}/a_{I,H_2O}$ is equal to 0.055^{22,23} under second explosion limit conditions.

We have concluded our analysis of the experimental data by adopting the "average" value $\alpha = 30$ and adjusting all the values of k_{eff} in the fourth column of Table III for the variable third-body effect indicated in Eq. (21) to arrive at the values of k_I^{Ar} recorded in the last column. Since these values of k_I^{Ar} decrease only slightly with increasing temperature, we further summarize the results by the average value $k_I^{Ar} = 1.42 \pm 0.24 \times 10^{15} \text{ cc}^2/\text{mole}^2 \text{ sec}$ at the midpoint of the temperature range, 1500°K.

DISCUSSION

The fundamental assumption in this work is that partial equilibrium is a valid approximation during

²² B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases* (Academic Press Inc., New York, 1961), p. 29.

²³ R. R. Baldwin and C. T. Brooks, *Trans. Faraday Soc.* **58**, 1782 (1962).

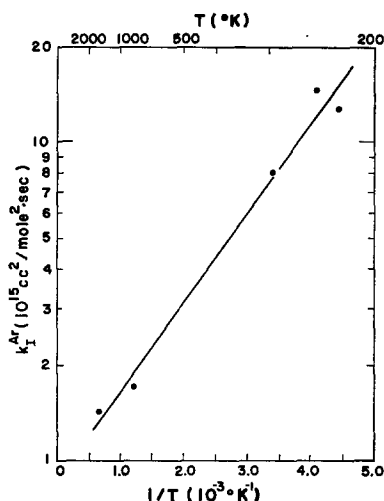


FIG. 6. Arrhenius plot of $\log_{10} k_I^{\text{Ar}}$ vs $1/T$ for results from 225° to 1850°K. Slope of line yields $-E_{\text{act}} = 1280 \pm 90$ cal/mole.

recombination between 1150° and 1850°K in the near-stoichiometric mixtures A-1 to A-6. Both the work of Kaskan⁴ and Schott⁵ and the consistent observation in these experiments that the peak OH concentrations were close to, but below the constant mole number value, support this assumption. In addition, computations using the best available values of the appropriate bimolecular rate constants²⁴⁻²⁶ indicate the validity of this approximation. Finally this conclusion is further supported by the results of these experiments, which are both internally consistent and in accord with independent observations.

These experiments have empirically confirmed the validity of Eq. (18), thus indicating that under these conditions the recombination process in lean mixtures is dominated by Reactions (I) and (III). In addition, experimental evidence strongly suggests that the contribution of Reaction (III) to Eq. (18) is negligible. It follows from this result and further analysis of the data that the contributions of the various species present in the reacting gas mixture to k_{eff} can be separated and values of k_I^{Ar} computed. Finally it appears to be a reasonable approximation to set $a_{\text{I,H}_2\text{O}} \sim 30$ at the experimental temperatures.

Our mean value of $k_I^{\text{Ar}} = 1.42 \times 10^{15}$ cc²/mole² sec at 1500°K can be combined with independent determinations made at other temperatures to obtain a rate expression over the range 225°–1850°K. The other values considered here are: (1) the results of Clyne and Thrush²⁰ at 225°K (12.7×10^{15}), 244°K (14.5×10^{15}), and 293°K (8.0×10^{15}), and (2) Baldwin's consensus value²¹ of 1.70×10^{15} at 813°K. The recent flame result

of Fenimore and Jones⁷ (1.0×10^{17} cc²/mole² sec at 1350°K for $M = \text{H}_2\text{O}$) was not included here because of the large uncertainty in $a_{\text{I,H}_2\text{O}}$ at these temperatures. In any case, however, it should be noted that with a H_2/O_2 ratio of 1.35 the magnitude of their rate constant might be deceptively large because of significant contributions from other recombination reactions such as (V).

An Arrhenius plot of $\log_{10} k_I^{\text{Ar}}$ against $1/T$ is presented in Fig. 6. Over the temperature range from 225° to 1850°K the experimental rate constants k_I^{Ar} can all be computed to within $\pm 20\%$ by the expression

$$k_I^{\text{Ar}} = 8.6 \times 10^{14} \exp(+1280 \pm 90/RT) \text{ cc}^2/\text{mole}^2 \text{ sec},$$

where the uncertainty in the exponent represents an estimated error (in the slope) in placing the best straight line through the data points.

Our estimates of $a_{\text{I,H}_2\text{O}}$ are in approximate agreement with the second explosion limit value of 32.0.²³ They are also in agreement with the relative efficiency of 24 ± 10 obtained by Clyne and Thrush²⁰ at 293°K. Thus our results offer some further support to the observation²⁰ that for Recombination Reaction (I), in contrast to the behavior of the iodine atom recombination reaction, the efficiencies of the various third bodies appear to be independent of temperature.

The present data can also be used to estimate upper limits for the rate constants of other recombination reactions that apparently cannot compete with (I) under these experimental conditions. Thus it is possible to assign such a limit to $k_{\text{III}}^{\text{Ar}}$ since Eq. (21) requires the condition that $k_I^{\text{Ar}} \gg K_{20} k_{\text{III}}^{\text{Ar}}$. If it is assumed that k_I^{Ar} and $k_{\text{III}}^{\text{Ar}}$ have the same temperature dependence between 1150° and 1850°K and that Eq. (21) is valid if $K_{20} k_{\text{III}}^{\text{Ar}} \leq 0.1 k_I^{\text{Ar}}$ at these temperatures a value of $k_{\text{III}}^{\text{Ar}} \leq 10^{15}$ cc²/mole² sec is obtained.

The observation that at $T > 1750^\circ\text{K}$ slopes of ~ 1.10 were obtained on curves similar to Figs. 3 and 4 indicates that early in the recombination period at high temperatures when $[\text{H}]$, $[\text{O}]$, and $[\text{OH}]$ are large, reactions other than (I) may be contributing significantly to the process. Recombination reactions (IV), (V), (VI), and (VIII) are the only ones that would produce a slope greater than one on a plot of this type. Since rate constants are available for (V),³ (VI),¹⁵ and (VIII)³ it is not difficult to show with Eqs. (13) and (14), assuming all $[C_j]$ are approximately equal, that they account for little of the enhanced rate of radical decay. It is thus possible to make a very crude estimate of the maximum value for k_{IV}^{M} . This can be done if on a plot similar to Fig. 3 the amount of $[-d\tau/dT]$ above that which would be predicted by a line with unit slope continued to larger $[\text{H}]$ from the region where k_{eff} was computed were assigned to Reaction (IV). In this manner Eqs. (13) and (14) have been used with this excess to compute that $k_{\text{IV}}^{\text{M}} \leq 10^{16}$ cc²/mole² sec.

²⁴ M. A. A. Clyne, Symp. Combust. 9th Ithaca, New York, 1962, 211 (1963).

²⁵ F. Kaufman and F. P. Del Greco, Symp. Combust. 9th Ithaca, New York, 1962, 659 (1963).

²⁶ R. R. Baldwin and A. Melvin, J. Chem. Soc. 1964, 1785.

CONCLUSIONS

Recombination in highly diluted, lean hydrogen-oxygen-argon mixtures with H_2/O_2 ratios of 0.50 and 0.33 has been studied over the temperature range 1150°–1850°K for reaction zone pressures of 0.85–5.14 atm. Under these conditions the partial equilibrium approximation is valid and the recombination process is dominated by Reaction (I). The rate coefficient $k_{I^{Ar}}$ was found to decrease slightly with temperature, but within the range covered in these experiments its variation was represented satisfactorily by a mean value of $1.42 \pm 0.24 \times 10^{15}$ cc²/mole² sec at 1500°K. This value has been combined with other experimental

determinations to obtain the expression $k_{I^{Ar}} = 8.6 \times 10^{14} \exp(+1280 \pm 90/RT)$ cc²/mole² sec for the entire temperature range from 225° to 1850°K. The efficiency of water relative to argon in promoting Reaction (I) has been estimated as approximately 30 at 1500°K.

ACKNOWLEDGMENTS

The authors wish to acknowledge the assistance of Charles W. Hamilton with the computer aspects of this problem and John G. Williamson and James L. Young in the performance of the experiments.

This work was performed under the auspices of the U.S. Atomic Energy Commission.

Electrical Properties of Ice. I. Dielectric Relaxation in Pure Ice

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(Received 29 April 1965)

The work of Onsager and Dupuis and of Jaccard on the motion of Bjerrum faults in an applied field is extended to include effects due to interactions between Bjerrum faults and to relaxation of the Bjerrum fault atmosphere.

I. INTRODUCTION

BEGINNING with Bjerrum's work in 1951,¹ considerable progress has been made in the understanding of the forces acting on ions in ice and of the mechanisms of conduction and dielectric relaxation. Especially important, from the theoretical point of view, have been the contributions of Jaccard² and of Onsager and Dupuis³ who have established the laws governing the motion of ions and Bjerrum faults in an applied field. The effects of interactions between particles (ions and Bjerrum faults) were not considered to any great extent by these authors.

Boyd,⁴ acting on a suggestion by Fuoss,⁵ has calculated the frictional force on an ion moving in a polar solvent which results from the dielectric relaxation induced by the ion's motion. Boyd's work has been generalized by Zwanzig.^{6,7} Both Boyd and Zwanzig make use of a macroscopic dielectric constant in their work.

The purpose of this paper is to generalize the work of Onsager and Dupuis and of Jaccard to include interactions between Bjerrum faults and effects on dielectric relaxation in pure ice. A later paper will deal with interactions between Bjerrum faults and ions and effects on the electrical conductivity. Comparisons with the continuum theory of Boyd and Zwanzig are made at the appropriate points.

II. EQUATIONS OF MOTION

The polarization vector is conveniently broken into two parts $\mathbf{P} = \mathbf{P}_0 + \mathbf{P}_\infty$, where \mathbf{P}_0 represents the contribution due to dipole orientation and \mathbf{P}_∞ represents the combined contributions of electronic and atomic polarization. For frequencies of interest, we can assume that \mathbf{P}_∞ follows the applied field perfectly. According to currently accepted ideas, \mathbf{P}_0 can change only through the migration of lattice defects, known as Bjerrum faults, which act as sources of the \mathbf{P}_0 field. Since the Bjerrum faults are charged particles they also serve as sources for the electric field \mathbf{E} . Equations expressing these relations have been given by Onsager and Dupuis:

$$\nabla \cdot \mathbf{E} = - (4\pi/\epsilon_\infty) \sum_i (e_i + q_i) \delta(\mathbf{r} - \mathbf{r}_i), \quad (1)$$

$$\nabla \cdot \mathbf{P}_0 = - \sum_i q_i \delta(\mathbf{r} - \mathbf{r}_i), \quad (2)$$

where q_i represents the Bjerrum charge on the i th

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