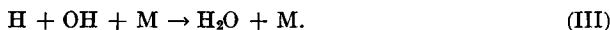
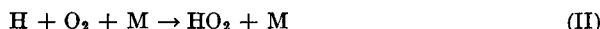


A SHOCK-WAVE STUDY OF RECOMBINATION IN NEAR-STOICHIOMETRIC HYDROGEN-OXYGEN MIXTURES

RICHARD W. GETZINGER

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico

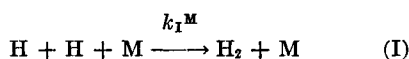
Recombination in very dilute hydrogen-oxygen-argon mixtures with H_2/O_2 ratios of 3:1 and 2.2:1 has been studied in a shock tube at 1307°–1846°K and 1.3–6.1 atm. The progress of the reaction was followed by OH ultraviolet line absorption. It was determined that recombination was third order in total pressure and that Reactions (I)–(III) were sufficient to account for the total rate of species disappearance.



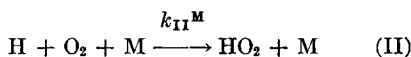
In the course of this analysis, the rate coefficient of Reaction (III), $k_{\text{III}}(\text{M} = \text{Ar})$, was determined to be $5.4 \pm 50\% \times 10^{15} \text{ cc}^2/\text{mole}^2 \text{ sec}$ at these temperatures. The results of this work and of previous recombination studies indicate that throughout the regime $8 \geq \text{H}_2/\text{O}_2 \geq 0.33$ recombination can be satisfactorily accounted for by only Reactions (I)–(III).

Introduction

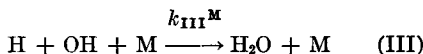
The shock-tube ultraviolet line-absorption experimental technique developed in this laboratory has recently been applied to the study of recombination in both fuel-rich¹ and fuel-lean² hydrogen-oxygen-diluent gaseous mixtures. By the utilization of the partial equilibrium approximation it was possible from the data obtained in these experiments to identify the reactions



and



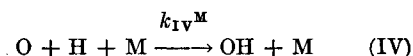
as being dominant in these two regimes, respectively. Small, but significant contributions from the reaction



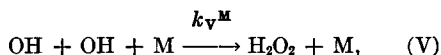
were also seen in the hydrogen-rich case. Values of the rate coefficients k_{I}^{Ar} and $k_{\text{II}}^{\text{Ar}}$ for Reactions (I) and (II) were reported at 1700° and 1500°K, respectively, and an estimate was made for the ratio $k_{\text{III}}^{\text{M}}/k_{\text{I}}^{\text{M}}$ at 1700°K in an atmosphere made up primarily of argon. These

results complement the previously reported observations made in flames.^{3–6}

The near-stoichiometric regime $2 \leq \text{H}_2/\text{O}_2 \leq 3$ has been largely neglected in these previous combustion studies. Under these conditions the enhanced relative importance of Reaction (III), as well as the possible participation of



and



presents an opportunity to obtain additional information about the high-temperature rate coefficients of simple radical recombination reactions. In the work described in this paper the shock-tube technique has been applied in a quantitative study of the recombination mechanism in this regime.

Experimental

The experimental method and apparatus for determining the concentration of hydroxyl radicals as a function of time behind an incident shock wave in gaseous hydrogen-oxygen mixtures highly diluted with argon have already been described in considerable detail² and were

TABLE I
Composition of experimental mixtures

Mixture	Ar	H ₂	O ₂	H ₂ /O ₂
A	98.00	1.50	0.50	3.0
B	97.00	2.25	0.75	3.0
C	97.60	1.65	0.75	2.2

unchanged for these experiments. The mixtures used in the present work are listed in Table I. The compositions were again verified mass spectrometrically. The mean temperatures (\bar{T}) and pressures (\bar{p}) for all experiments were between 1307° and 1846°K, and 1.3 and 6.1 atm, respectively. These conditions were obtained by driving 6–24 cm Hg of mixtures A–C with 75–330 psia of hydrogen gas. Radiation emitted from the reacting gases in the shock tube was observed to be negligible compared to the flash lamp output in the wavelength interval of interest in mixture A and assumed to be so for mixtures B and C.

Results

The data relating $[\text{OH}]$ to laboratory time τ for each experiment were treated exactly as described previously.² Thus, the partial equilibrium approximation was used to obtain the concentrations of the other six species Ar, H₂, O₂, H₂O, H, and O for each experimentally determined $[\text{OH}]$. Similarly, values of the non-dimensional progress variable ν , which is equal to 1 at partial equilibrium with no recombination and 0 at full equilibrium, were determined for each $[\text{OH}]$. For each experiment, a smooth curve relating $\ln \nu$ and $\ln \tau$ in a quadratic expression was obtained by applying a least-squares fitting procedure to the data. Slopes, $d\nu/d\tau$, were computed from the equations for these curves for the ν representing each experimental OH concentration, and at other convenient common values of ν selected as points of comparison between experiments.

The basic expression used in interpreting these results has been derived previously² and will be written here as

$$-(p_0/RT_0)(1 - N_{\text{eq}})(d\nu/d\tau) = R_{\text{rec}} \\ = \sum_{j=1}^I k_j^{\text{eff}}[A_j][B_j][\text{Ar}] \quad (1)$$

in anticipation that the dominant third body in mixtures A–C will be the inert diluent. In Eq. (1), p_0 and T_0 are the pressure and temperature of the unshocked gas, N_{eq} the total moles in the system at full equilibrium per initial mole, R_{rec} the sum of the net forward rates of all l recombination reactions, $[A_j]$ and $[B_j]$ the concentrations of the two reactive species involved in reaction j , and k_j^{eff} is defined by

$$k_j^{\text{eff}} = \frac{k_j^{\text{Ar}}}{[\text{Ar}]} \sum_{i=1}^7 a_{ji}[I]. \quad (2)$$

a_{ji} is the efficiency of species I relative to Ar in promoting reaction j . The summation in Eq. (2) is over all seven species. The objective of the analysis carried out in the following paragraphs is to determine which recombination reactions are the important contributors to R_{rec} in Eq. (1) under the conditions of these experiments.

It should be noted that Eq. (1) contains the implicit assumption that only termolecular recombination reactions are important in these experiments. As demonstrated elsewhere,² this assumption can be checked by examining the dependence of $(-d\nu/d\tau)$ taken at a fixed ν upon the initial pressure for a series of experiments with the same initial composition and mean temperature (\bar{T}). Figure 1 is a logarithmic plot of $-d\nu/d\tau$ at $\nu = 0.40$ versus p_0 for twelve experiments carried out in mixture C at approximately 1650°K. A fourfold range in initial pressure is covered by these experiments. The line on the graph represents the result of a least-squares fit of the data points and has a slope of 2.15 with a standard deviation of ± 0.12 . A similar plot for these same twelve experiments at $\nu = 0.45$ yielded a least-squares slope of 1.98 ± 0.08 .

Other slopes have been obtained by this procedure from experiments in mixture A. Shock velocities, and therefore temperatures, were carefully matched in eight experiments with initial pressures of 6–18 cm Hg at 1725°K. Slopes of 1.89 ± 0.14 and 1.91 ± 0.13 were obtained at $\nu = 0.40$ and 0.30 , respectively. Within the uncertainties inherent in this approach these slopes are all essentially equal to 2, the value predicted by Eq. (1).

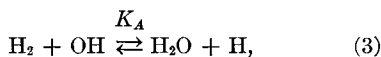
The consistency of the slopes determined in this manner over various experimental conditions affords considerable evidence for the validity of the measurement and analysis techniques, as well as of the assumption regarding three-body recombination reactions. In view of the results of previous high-temperature studies of recombination it would have been quite surprising if slopes other than two could be traced to the participa-

tion of bimolecular recombination reactions rather than to errors in the method of taking or reducing the data. The present results provide no reason to suspect either the data or the validity of Eq. (1) for its interpretation.

Figure 1 also illustrates the dynamic range over which the OH absorption technique is capable of making rate measurements. Whereas for termolecular recombination the derivative $-d\nu/d\tau$ is proportional to p_0^2 , under similar conditions the quantity $-d[\text{OH}]/d\tau$ is proportional to p_0^3 [for example, see Eq. (15) of Ref. 1]. Since in Fig. 1 the rate $-d\nu/d\tau$ increases by a factor of approximately 16 for a fourfold increase in the initial pressure, the corresponding slopes $-d[\text{OH}]/d\tau$ are a factor of 64 apart. This factor is essentially the ratio of the maximum to the minimum slopes that can be measured with this technique.

Now that it has been established that only termolecular reactions need be considered in the analysis, it is possible to proceed with the determination of which such reactions are the important ones. A complete list of the only likely participating reactions appears in Ref. 2. Consideration of the relative concentrations in these near-stoichiometric mixtures and of the approximate rate coefficients makes it quite apparent that Reactions (I)–(V) (in the present notation) are the only ones from which significant contributions to R_{rec} might be expected under the experimental conditions.

A preliminary estimate of the relative importance of these five reactions in the experiments can be obtained from recombination data for mixtures A and B. Since in these 3:1 mixtures $[\text{H}_2]$ and $[\text{H}_2\text{O}]$ are approximately constant throughout $1 \geq \nu \geq 0$, $[\text{OH}]$ and $[\text{H}]$ are proportional to each other because of the partial equilibrium relationship



$$[\text{H}] = (K_A[\text{H}_2]/[\text{H}_2\text{O}])[\text{OH}]. \quad (4)$$

Thus, any combination of Reactions (I), (III), and (V) would indicate that for a given experiment

$$-d\nu/d\tau \propto [\text{OH}]^2, \quad (5)$$

while, from similar equilibrium considerations, Reactions (II) and (IV) would predict a rate proportional to $[\text{OH}]^3$.

Logarithmic plots of $-d\nu/d\tau$ against $[\text{OH}]$ for all 3:1 experiments consistently yielded slopes

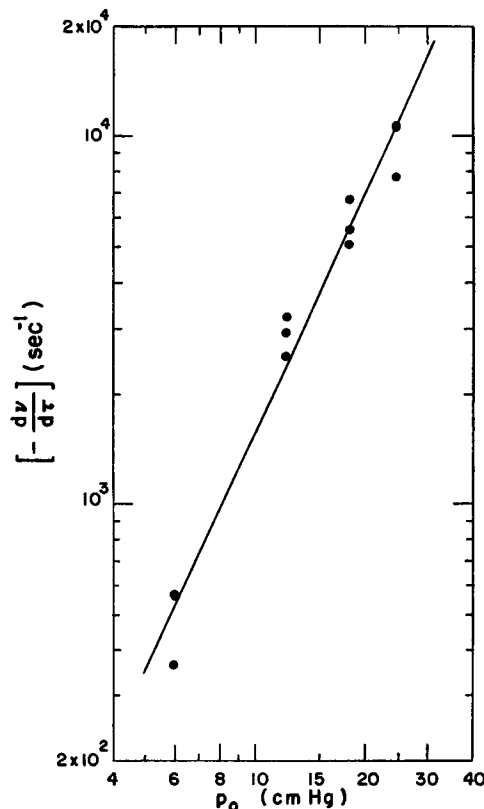


FIG. 1. Effect of total pressure upon recombination rate. Mixture C, $\nu = 0.40$, and $\bar{T} \approx 1650^\circ\text{K}$. Slope of line determined by least-squares fit = 2.15 ± 0.12 .

close to 2, indicating that Reactions (II) and (IV) are only of minor importance under these conditions. Similar reaction order considerations cannot be applied to mixture C since $[\text{H}_2]$ and $[\text{H}_2\text{O}]$ are both far from being constants under these very nearly stoichiometric conditions. Because significant participation of several termolecular reactions in the recombination mechanism was expected under these conditions, no attempt was made to establish an empirical rate law by logarithmically plotting $-d\nu/d\tau$ against various reaction concentration products $[A_j][B_j]$.

Because the experimental results do not lend themselves to interpretation by these direct methods of analysis, it is necessary to find another, more general, and correspondingly more indirect means of investigating the reaction mechanism. The approach developed in this work makes use of the fact that the rate coefficients k_{I}^{Ar} and $k_{\text{II}}^{\text{Ar}}$ are now reasonably well known at these temperatures. For this purpose, it is

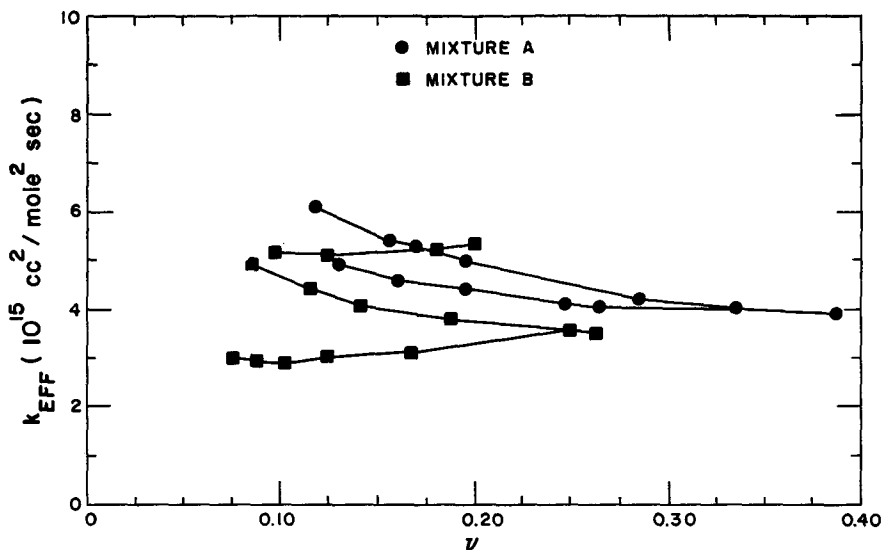


FIG. 2. Dependence of k_{EFF} on ν for five experiments in 3:1 mixtures. Mixture A experiments: $p_0 = 18$ cm Hg, $\bar{T} \approx 1700^\circ\text{K}$, and $\bar{p} \approx 4.4$ atm. Mixture B experiments: $p_0 = 15$ cm Hg, $\bar{T} \approx 1830^\circ\text{K}$, and $\bar{p} \approx 3.9$ atm.

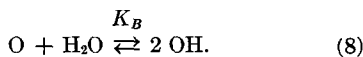
necessary to rearrange Eq. (1) to the form

$$\begin{aligned}
 &-(p_0/RT_0)(1 - N_{\text{eq}})(d\nu/d\tau) - k_{\text{I}}^{\text{eff}}[\text{H}]^2[\text{Ar}] \\
 &- k_{\text{II}}^{\text{eff}}[\text{H}][\text{O}_2][\text{Ar}] \\
 &\equiv \Delta = k_{\text{EFF}}[\text{H}][\text{OH}][\text{Ar}], \quad (6)
 \end{aligned}$$

where

$$\begin{aligned}
 k_{\text{EFF}} &= k_{\text{III}}^{\text{eff}} \\
 &\times \left[1 + \frac{k_{\text{IV}}^{\text{eff}}}{k_{\text{III}}^{\text{eff}}} K_B^{-1} \frac{[\text{OH}]}{[\text{H}_2\text{O}]} + \frac{k_{\text{V}}^{\text{eff}}}{k_{\text{III}}^{\text{eff}}} K_A^{-1} \frac{[\text{H}_2\text{O}]}{[\text{H}_2]} \right], \quad (7)
 \end{aligned}$$

and



Thus contributions to R_{rec} from Reactions (III)–(V) are combined in an effective coefficient, k_{EFF} , while the difference Δ represents what remains after the rates of Reactions (I) and (II) have been subtracted from R_{rec} . Values of k_{EFF} and Δ can be computed from Eq. (6) for each experimentally determined $[\text{OH}]$. If Δ is a large fraction of R_{rec} , its variation, or that of k_{EFF} , with experimental conditions can be used to assess reliably the relative importance of each of the remaining Reactions (III)–(V).

In the analysis carried out in the following paragraphs, k_{EFF} was used for this purpose.

The feasibility of the approach just described depends of course upon the relative magnitudes of R_{rec} and Δ . To obtain values of Δ and also k_{EFF} , it is necessary to know $k_{\text{I}}^{\text{eff}}$ and $k_{\text{II}}^{\text{eff}}$. These effective coefficients are, in turn, functions of k_{I}^{Ar} and $k_{\text{II}}^{\text{Ar}}$, the relative efficiencies $a_{\text{I},i}$ and $a_{\text{II},i}$, and the concentrations $[I]$, as formulated in Eq. (2). For the results described below, k_{I}^{Ar} was taken as 4×10^{14} cc²/mole² sec,¹ $k_{\text{II}}^{\text{Ar}}$ as 1.42×10^{15} cc²/mole² sec,² $a_{\text{I},\text{H}_2\text{O}}$ and a_{I,H_2} as 5.0,¹ $a_{\text{II},\text{H}_2\text{O}}$ as 30,² and a_{II,H_2} as 5.0.⁷ The concentrations used were, of course, those computed for partial equilibrium at each measured $[\text{OH}]$. Contributions of the third bodies O_2 , OH , H , and O to $k_{\text{I}}^{\text{eff}}$ and $k_{\text{II}}^{\text{eff}}$ under these conditions were ignored because their concentrations were very small in comparison with $[\text{Ar}]$ and $[\text{H}_2\text{O}]$ throughout the ν regime in which nearly all of the data were taken ($\nu \leq 0.40$).

The quantities Δ and k_{EFF} have been computed at various values of ν for each of the experiments in which a significant change in $[\text{OH}]$ was seen over a period of 400–500 μsec . A total of 27 experiments in mixtures A and B and 25 experiments in mixture C met this qualification. The only experiments discarded were those few at $\bar{T} < 1400^\circ\text{K}$ or $\bar{p} < 1.5$ atm. In mixtures A and B the percentage of recombination to be accounted for by Reactions (III)–(V), $100(\Delta/R_{\text{rec}})$, was nearly always in

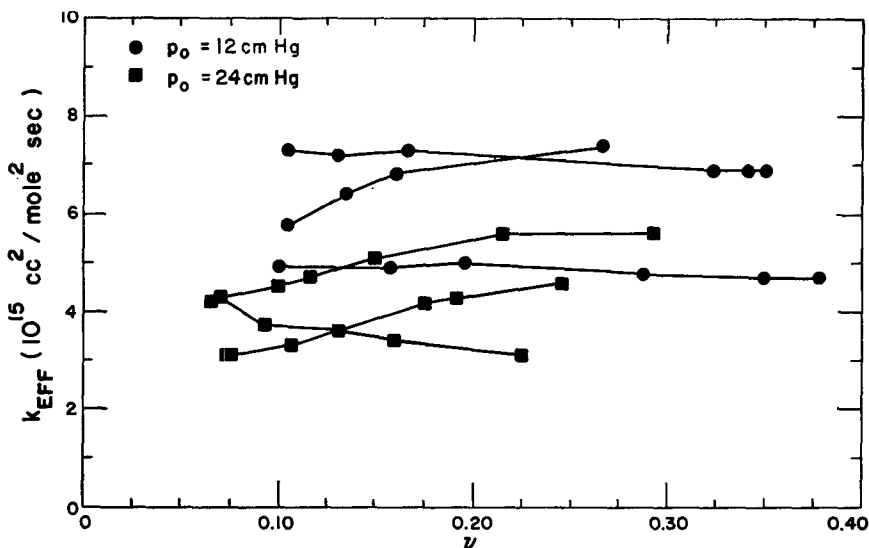


FIG. 3. Dependence of k_{EFF} on ν for six experiments at two different pressures in mixture C. 12 cm Hg experiments: $\bar{T} \approx 1660^\circ\text{K}$, and $\bar{p} \approx 2.7$ atm. 24 cm Hg experiments: $\bar{T} \approx 1650^\circ\text{K}$, and $\bar{p} \approx 5.5$ atm.

TABLE II

Summary of experimental results*

\bar{T}	No. of expts.	\bar{p}	ν	[OH]	[H]/[OH]	No. of k_{EFF} 's computed	Maximum-minimum k_{EFF}	Mean k_{EFF} ($\approx k_{\text{III}}^{\text{Ar}}$)
<i>Mixture A:</i>								
1400-1700	4	3.6-4.3	0.34-0.12	9.3-1.9	14.9-8.2	24	11.9-4.0	8.2
1700-1800	7	1.5-4.4	0.39-0.12	11.0-2.8	8.2-7.3	26	8.9-3.9	5.5
	11†					50†		6.8‡
<i>Mixture B:</i>								
1500-1700	4	3.0-3.5	0.29-0.08	10.1-2.5	12.8-8.1	19	8.2-2.6	5.4
1700-1800	9	1.8-5.5	0.39-0.05	11.1-3.1	7.9-6.4	39	12.5-1.9	4.7
1800-1900	3	3.9	0.26-0.08	12.4-3.9	6.2-5.6	15	5.3-2.9	4.0
	16†					73†		4.7‡
<i>Mixture C:</i>								
1400-1600	6	2.8-5.0	0.37-0.08	17.1-4.5	7.8-3.0	32	18.4-2.8	6.8
1600-1700	13	2.7-5.6	0.38-0.06	19.3-5.2	4.5-2.1	68	8.6-1.5	5.0
1700-1900	6	3.9-6.1	0.40-0.05	23.5-9.2	2.9-1.5	28	5.7-1.9	4.2
	25†					128†		5.3‡

* Units: \bar{T} in degrees Kelvin, \bar{p} in atmospheres, [OH] in 10^{-6} moles/liter, and k_{EFF} in 10^{15} cc²/mole² sec

† Total for mixtures.

‡ Average value for mixture.

the range $50 \pm 10\%$, with Reaction (I) making up essentially all of the remaining amount. In mixture C this percentage was $60 \pm 10\%$, with Reaction (II) contributing slightly more of the remainder than Reaction (I). Actually, mixture (C) was carefully chosen to optimize this percentage. It is felt that these percentages are large enough to warrant use of this approach in the further analysis of the data.

Some typical results of the calculations are shown in Figs. 2 and 3. In these graphs, k_{EFF} is plotted as a function of ν for one or more sets of experiments in each mixture. The line segments connect points common to a given experiment. The conclusion drawn from these and similar graphs for other experiments is that although the computed values of k_{EFF} show a considerable amount of scatter, within a given experiment they are independent of the progress variable ν , at least for $\nu < 0.40$.

Use has been made of this observation in preparing Table II, which summarizes all of the experimental results. In this tabulation, Column 1 indicates the temperature range into which the number of experiments given in Column 2 fell. The next four columns show the range in reaction zone pressures, ν values, observed hydroxyl radical concentrations, and $[\text{H}]/[\text{OH}]$ ratios involved in the computations of k_{EFF} for these experiments. Column 7 gives the total number of k_{EFF} 's calculated, Column 8 the range covered by these coefficients, and Column 9 their average value.

Table II indicates that within the scatter of the data there is no difference between values of k_{EFF} obtained from the three mixtures. It is also apparent that the dependence of k_{EFF} upon temperature within each mixture is slight, or possibly nonexistent. Thus, the mean value of $5.4 \times 10^{15} \text{ cc}^2/\text{mole}^2 \text{ sec}$ ($\pm 50\%$ would include 80% of the data) will be used to describe all of the computed coefficients.

Having described the observed behavior of k_{EFF} , it is now of interest to reexamine Eq. (7) in light of these observations to see what can be learned about the relative importance of Reactions (III)–(V) in the experiments. It is apparent that for a given experiment all quantities on the right-hand side of this equation are essentially constant except the ratios $[\text{OH}]/[\text{H}_2\text{O}]$ and $[\text{H}_2\text{O}]/[\text{H}_2]$. In addition, as explained earlier, for experiments in mixtures A and B, $[\text{H}_2\text{O}]$ and $[\text{H}_2]$ are also independent of ν . Thus, for any particular experiment in these two mixtures the behavior of k_{EFF} can be described by

$$k_{\text{EFF}} = \alpha + \beta[\text{OH}], \quad (9)$$

where α and β are constants which reflect the relative contributions to k_{EFF} of Reactions (III) and (V), and Reaction (IV), respectively.

$$\alpha = k_{\text{III}}^{\text{eff}} \times \{1 + (k_{\text{V}}^{\text{eff}}/k_{\text{III}}^{\text{eff}}) K_A^{-1} ([\text{H}_2\text{O}]/[\text{H}_2])\} \quad (10)$$

and

$$\beta = k_{\text{IV}}^{\text{eff}}/K_B[\text{H}_2\text{O}]. \quad (11)$$

Since as ν approaches 0 during an experiment, $[\text{OH}]$ is also decreasing toward its value at full equilibrium, Eq. (9) indicates that the computed k_{EFF} 's should diminish toward some limiting value α as recombination proceeds. Therefore, a graph of k_{EFF} versus $[\text{OH}]$, or ν , will yield information regarding the relative magnitudes of the quantities α and β in Eq. (9).

Figure 2 is such a graph. Shown here are five experiments in which $[\text{OH}]$ decreases by a factor of between 1.9 and 3.0 during the indicated changes in ν . As stated earlier, other experiments, in which $[\text{OH}]$ decreases by a factor as large as 3.5, also show no consistent dependence upon ν . It would appear that, at least in mixtures A and B, the contribution of Reaction (IV) to k_{EFF} is of minor importance. The approximation will therefore be made that in these mixtures $k_{\text{EFF}} \approx \alpha$.

Use is now made of the observed behavior of k_{EFF} for a changing \bar{T} in mixtures A and B to determine the relative contributions of Reactions (III) and (V) to α . Of the quantities on the right-hand side of Eq. (10) only K_A is a significant function of \bar{T} under the conditions of these experiments. This is so because (a) the coefficients $k_{\text{III}}^{\text{eff}}$ and $k_{\text{V}}^{\text{eff}}$ are expected to be essentially independent of temperature, and (b) the ratio $[\text{H}_2\text{O}]/[\text{H}_2]$ is approximately a constant over the entire experimental range of temperatures and ν values. In fact partial equilibrium computations for these 3:1 mixtures clearly demonstrate that the quantity $[\text{H}_2\text{O}]/[\text{H}_2]$ is approximately equal to 2, its value at full equilibrium throughout $1 \geq \nu \geq 0$ at these temperatures. Thus, the contribution of Reaction (V) to α should be largest at the temperature at which K_A is smallest.

Between 1400° and 1800°K , K_A decreases by a factor of 3.4 (48 to 14).⁸ However, Table II indicates that, if anything, k_{EFF} decreases slightly for a similar 400°K change in temperature. It therefore seems certain that the contribution of Reaction (V) to α , if not negligible, is at least minor. Thus, it appears appropriate to set $k_{\text{EFF}} \approx \alpha \approx k_{\text{III}}^{\text{eff}}$. It should be realized

that this value of $k_{\text{III}}^{\text{eff}}$ may include small contributions from Reactions (IV) and (V), as well as from errors in the coefficients $k_{\text{I}}^{\text{eff}}$ and $k_{\text{II}}^{\text{eff}}$ used in Eq. (6).

Additional evidence for the approximate equality of k_{EFF} and $k_{\text{III}}^{\text{eff}}$ can be obtained from experiments carried out in mixture C. Here, k_{EFF} is also independent of ν (Fig. 3) and at any given temperature (see Table II) its value is essentially the same as in mixtures A and B. This must mean that the second and third terms within the bracket in Eq. (7) are quite small compared with 1 in all of the experiments, since at a fixed temperature and any common ν both ratios $[\text{OH}]/[\text{H}_2\text{O}]$ and $[\text{H}_2\text{O}]/[\text{H}_2]$ are considerably larger in mixture C than in the 3:1 mixtures. Thus, the fact that k_{EFF} is independent of the mixture composition supports the conclusion that $k_{\text{EFF}} \approx k_{\text{III}}^{\text{eff}}$.

As a final step in this analysis, consideration is now given to obtaining a value for $k_{\text{III}}^{\text{Ar}}$ from $k_{\text{III}}^{\text{eff}}$. This problem is complicated by the fact that no information is available on the efficiencies of third bodies relative to argon in promoting Reaction (III) at these temperatures. However, since mixtures A-C contain $\geq 97\%$ argon, a reasonably accurate value of $k_{\text{III}}^{\text{Ar}}$ can be obtained by simply setting $k_{\text{III}}^{\text{Ar}} = k_{\text{III}}^{\text{eff}} = 5.4 \times 10^{15} \text{ cc}^2/\text{mole}^2 \text{ sec}$.

Discussion

The main result of this work is the conclusion that throughout the near-stoichiometric region, and, indeed, throughout the entire regime $8 \geq \text{H}_2/\text{O}_2 \geq 0.33$, recombination in hydrogen-oxygen-diluent mixtures can be satisfactorily accounted for by only Reactions (I)-(III). The first part of this statement has been tested in the following additional ways:

(a) Computations to obtain k_{EFF} from Eq. (6) have been repeated for selected experiments using what are considered extreme values of k_{I}^{Ar} and $k_{\text{II}}^{\text{Ar}}$. These limits were determined by carefully evaluating the available rate-coefficient data,^{1,2,9} and are, in the first case, $k_{\text{I}}^{\text{Ar}} = 6.0 \times 10^{14}$ and $k_{\text{II}}^{\text{Ar}} = 1.7 \times 10^{15}$, and, in the second, $k_{\text{I}}^{\text{Ar}} = 2.0 \times 10^{14}$ and $k_{\text{II}}^{\text{Ar}} = 1.2 \times 10^{15}$. All of these coefficients are in units of $\text{cc}^2/\text{mole}^2 \text{ sec}$.

The resulting values of k_{EFF} , although displaced slightly from the previous levels, show essentially the same behavior with respect to ν , \bar{T} , and composition as indicated earlier, and fall well within the error limits previously prescribed ($5.4 \pm 50\% \times 10^{15}$). Thus, it appears that even assigning reasonable error limits to the rate coefficients for Reactions (I) and (II) does not alter the fact that there is a significant residual

contribution to R_{rec} that cannot be accounted for by these reactions and that this residual can be traced to Reaction (III).

(b) Estimates have been made of the maximum values of $k_{\text{IV}}^{\text{eff}}$ and $k_{\text{V}}^{\text{eff}}$ that are consistent with the assumption of negligible participation of Reactions (IV) and (V) in the recombination process. For this purpose, the second and third terms within the bracket of Eq. (7) were equated to 0.2 at their maximum value in the 3:1 experiments. Thus, in a particular low-temperature experiment (1474°K) in which K_B is correspondingly quite small (estimated by interpolation as 3.3×10^{-2}),⁸ and at a high ν value ($\nu = 0.32$), at which the ratio $[\text{OH}]/[\text{H}_2\text{O}]$ is largest ($= 1.86 \times 10^{-2}$), it was determined that to be consistent with the conclusions stated earlier $k_{\text{IV}}^{\text{eff}}$ must be no larger than $0.35k_{\text{III}}^{\text{eff}}$ ($\leq 2 \times 10^{15} \text{ cc}^2/\text{mole}^2 \text{ sec}$). Similarly, at a high temperature (1726°K), with minimum $K_A \approx 17$,⁸ and with $[\text{H}_2\text{O}]/[\text{H}_2] \approx 2$, it was determined that $k_{\text{V}}^{\text{eff}}$ must be $\leq 1.7k_{\text{III}}^{\text{eff}}$ ($\leq 9 \times 10^{15} \text{ cc}^2/\text{mole}^2 \text{ sec}$). Since the rate coefficients $k_{\text{IV}}^{\text{eff}}$ and $k_{\text{V}}^{\text{eff}}$ would have to be large to exceed these limits, it is not surprising that Reactions (IV) and (V) play no significant role in these recombination experiments.

The following general comments regarding the experimental approach would appear to be appropriate at this time:

(a) The fact that the partial equilibrium approximation has been satisfactorily employed in the interpretation of recombination in mixtures that were both richer¹ and leaner² than those studied in the present experiments is confirmation of its validity in this work. This approximation fails where there are large excesses of hydrogen or oxygen in the product mixture due to an extreme initial H_2/O_2 ratio. These excesses (i) delay the initial approach to partial equilibrium, and (ii) may make impossible the attainment of a satisfactory proximity to it at any ν value achieved on the time scale of experiments such as these. Both of these effects are produced because the concentrations of particular intermediate species are reduced to very low levels by extreme amounts of either H_2 or O_2 . As a result, for a large excess of either reactant, the forward and reverse rates of at least one of the key bimolecular reactions are reduced to the point where the rate of approach to a partial equilibrium condition is slow compared to the perturbation introduced by rapid recombination reactions. Under these extreme conditions, equilibrium is not reached until sufficient recombination has occurred to deplete the largest atom and radical concentrations to the point where the appropriate termolecular

reactions are also quite slow. Such equilibration may not be seen during the limited observation time available in a shock-tube experiment.

(b) The limits on the ν values for which computations of k_{EFF} were made are given in Table II. They were arbitrarily determined in the following manner: Plots of ν versus τ were made for each group of three or four experiments carried out under identical conditions. These points form a curve relating ν and τ for those particular experimental conditions. It was observed on such graphs that most of the data fell within a certain limited range in ν and τ . Points were selected from this region for computational purposes, since the fit provided by the $\ln \nu$ versus $\ln \tau$ quadratic was best for these particular values. Because $[\text{OH}]$ is quite insensitive to ν above $\nu \approx 0.5$ few points were observed with large ν values.

(c) The computed temperature changes during the recombination experiments ($\nu = 1$ to $\nu = 0$) were as follows: mixture A, $\approx 90^\circ\text{K}$; mixture B, $\approx 130^\circ\text{K}$; and mixture C $\approx 130^\circ\text{K}$.

The value obtained here for $k_{\text{III}}^{\text{Ar}}$ is in good agreement with that reported by Schott and Bird¹ for $k_{\text{III}}^{\text{M}}$ ($= 6 \pm 3 \times 10^{15}$ cc²/mole² sec), where M is an atmosphere of $\geq 91\%$ argon. Apparently, no other values of $k_{\text{III}}^{\text{Ar}}$ are available at these temperatures.

ACKNOWLEDGMENTS

I am pleased to acknowledge many helpful discussions with Dr. Garry L. Schott concerning the

background and problems associated with this work. In addition, I greatly appreciate the assistance of Mr. Larry S. Blair in the reduction of data and Mr. James L. Young and Mr. John G. Williamson in the performance of the experiments.

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

REFERENCES

1. SCHOTT, G. L. AND BIRD, P. F.: J. Chem. Phys. **41**, 2869 (1964).
2. GETZINGER, R. W. AND SCHOTT, G. L.: J. Chem. Phys. **43**, 3237 (1965).
3. DIXON-LEWIS, G., SUTTON, M. M., AND WILLIAMS, A.: Discussions Faraday Soc. **33**, 205 (1962), and Tenth Symposium (International) on Combustion, p. 495, The Combustion Institute, 1965.
4. ROSENFELD, J. L. J. AND SUGDEN, T. M.: Combust. Flame **8**, 44 (1964).
5. KASKAN, W. E.: Combust. Flame **2**, 286 (1958).
6. FENIMORE, C. P. AND JONES, G. W.: Tenth Symposium (International) on Combustion, p. 489, The Combustion Institute, 1965.
7. LEWIS, B. AND VON ELBE, G.: Combustion, Flames and Explosions of Gases, p. 29, Academic Press, 1961.
8. JANAF Thermochemical Tables, Dow Chemical Co., Midland, Michigan, August, 1965.
9. LARKIN, F. S. AND THRUSH, B. A.: Tenth Symposium (International) on Combustion, p. 397, The Combustion Institute, 1965.