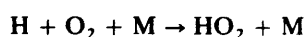
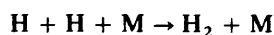


RECOMBINATION IN THE HYDROGEN-OXYGEN REACTION: A SHOCK TUBE STUDY WITH NITROGEN AND WATER VAPOUR AS THIRD BODIES*

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Previous shock tube studies of termolecular recombination in the hydrogen-oxygen reaction have been extended to mixtures containing significant amounts of nitrogen or water vapour. An OH ultra-violet line absorption technique has been used to follow the progress of the overall reaction at temperatures of 1259° to 1912°K and pressures of 1.1 to 3.7 atm. Selective variation of the initial composition, which for the water vapour experiments required the development of a special flow-fill apparatus to introduce up to 7.9 per cent water vapour into the unshocked gas mixtures, has made possible a determination of the effect of both of these species as third bodies on the three important recombination reactions:



and

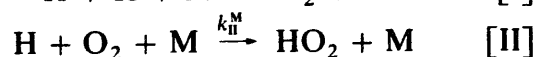
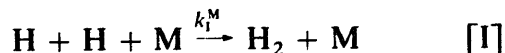


Results in mixtures diluted with nitrogen indicate that the rate coefficients of each of these reactions with the third body $\text{M} = \text{N}_2$ are approximately 1.5 times the values previously reported for $\text{M} = \text{Ar}$. Determination of the water vapour coefficients is complicated by the presence of other important third bodies, i.e. argon and hydrogen or oxygen. However, the results show that water vapour is an efficient catalyst in bringing about recombination. The ratio of rate coefficients for $\text{M} = \text{H}_2\text{O}$ to those with $\text{M} = \text{Ar}$ for these three reactions is ≤ 13 , 25, and 20, respectively.

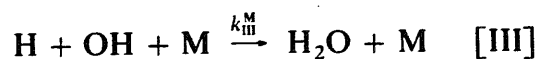
It is now well-established that concentrations of the intermediates H, O and OH far in excess of their equilibrium values are produced during the course of the explosive chain reaction between gaseous hydrogen and oxygen at moderate temperatures. These overshoots are a direct result of the separation in time between the rapid bimolecular, chain propagation steps, and the slow, three-body recombination reactions that eventually bring the system to equilibrium. Equilibration of the bimolecular propagation steps actually takes place during the final, recombination-limited stage of the reaction and the system passes through a series of 'partial equilibrium' states^{1,2} as full equilibrium is approached. For low-to-moderate densities and a wide range of initial hydrogen/oxygen ratios the system is partially equilibrated through

essentially all of the recombination portion of the reaction. The termolecular recombination reactions are responsible for the net decrease in the total moles of reactant species required by the overall stoichiometry $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$, and for the release of the bulk of the latent chemical energy of the complete reaction.

The mechanism of recombination in this system is now quite well understood as a result of a number of recent investigations in both premixed flames³⁻⁶ and shock tubes^{2, 7, 8}. Only three termolecular reactions:



and



contribute significantly to recombination in mixtures with initial hydrogen/oxygen ratios²

* An abbreviated account of this work was presented at the Sixth International Shock Tube Symposium, Freiburg, West Germany, April 1967.

between 8 and 0.33. The HO_2 formed in reaction II is rapidly removed in essentially irreversible bimolecular reactions that do not change the total number of moles in the system⁸.

Fundamental information concerning the rate of recombination, i.e. the rate coefficients for reactions I–III, is much more difficult to obtain. Interest in this subject has been generated not only by the potential usefulness of hydrogen as a fuel, but also because of the importance of these reactions in other oxidation processes^{9, 10}. Reduction of data taken in combustion studies to elementary coefficients k_j^M is greatly complicated by the presence of a number of chaperons, M, whose contributions to the total recombination rate must be separated. This problem has been largely overcome in the shock tube investigations by making use of high dilution of the reactants with argon to obtain values of $k_1^{\text{Ar}}-k_{\text{III}}^{\text{Ar}}$. The use of dilution in flame studies in hydrogen–oxygen–nitrogen mixtures has been hindered by the necessity of restricting experimental conditions to those required for a stable flame configuration. As a result there is considerable uncertainty in the important coefficients $k_1^{\text{N}_2}$, $k_{\text{III}}^{\text{N}_2}$, $k_1^{\text{H}_2\text{O}}-k_{\text{III}}^{\text{H}_2\text{O}}$, $k_1^{\text{H}_2}$ and $k_{\text{III}}^{\text{H}_2}$ obtained in these studies. Experimental values of the coefficients k_1^{Ar} , $k_{\text{III}}^{\text{Ar}}$ and $k_1^{\text{H}_2}$ are also available from high temperature dissociation studies of hydrogen^{11–13} and water vapour¹⁴.

Because of the importance of the coefficients for $\text{M} = \text{N}_2$ and H_2O in practical combustion systems it was decided to extend the shock tube technique to hydrogen–oxygen–nitrogen and hydrogen–oxygen–argon–water vapour mixtures containing significant amounts of these particular species. This paper reports values of the elementary rate coefficients obtained in such an investigation.

Experimental

Recombination data were obtained by shocking dilute hydrogen–oxygen–nitrogen, hydrogen–oxygen–argon, and hydrogen–oxygen–argon–water vapour mixtures to the temperatures and pressures used in previous shock tube experiments. These data consisted of measurements for each experiment of: (a) the speed of the incident shock wave, and (b) ultra-violet absorption by the OH radical as a function of time

behind this wave. The shock tube and optical setup used in these experiments remained essentially the same as that described previously⁸. Some additional equipment was required for the preparation of reactant mixtures containing water vapour.

Three hydrogen–oxygen–nitrogen mixtures were used in the course of this work: 1.0% H_2 –3.0% O_2 –96.0% N_2 , 1.65% H_2 –0.75% O_2 –97.6% N_2 , and 6.0% H_2 –1.0% O_2 –93.0% N_2 . Experimental conditions in the first two of these mixtures were selected to facilitate comparison of the results with those reported previously for experiments in similar argon mixtures^{2, 8}. A further comparison of results was made possible by the choice of similar experimental conditions for the third mixture and for experiments carried out in a 6.0% H_2 –1.0% O_2 –93.0% Ar mixture. For reasons given later in the Discussion section the pressure broadening parameter, a , used in the analysis of the nitrogen experiments was taken as $350 \bar{p}$ (atm)/ \bar{T} (°K), where \bar{p} and \bar{T} are the mean pressure and temperature of each experiment. Otherwise all of these experiments were treated by the same method of reducing the velocity and absorption data to $[\text{OH}]/\text{time}$ profiles described previously⁸. In these experiments \bar{p} and \bar{T} were held between 2.0 and 2.8 atm, and 1306° and 1912°K.

Hydrogen–oxygen–argon–water vapour gas mixtures were prepared by flow-filling the expansion section of the shock tube using the apparatus shown schematically in Figure 1. Dilute mixtures of hydrogen and oxygen in argon at pressures up to 100 lb/in² abs. were first prepared separately using a special high pressure manifold. The resulting gas mixture was expanded from the high pressure cylinder through a pressure regulator and needle valve V5 before flowing slowly over ice and through the shock tube expansion section. The effluent gas left the shock tube at a point near the diaphragm and was exhausted through a vacuum pump to the atmosphere. The flowrate through the shock tube was controlled by V5 at approximately 1.0 standard cubic foot per minute (scfm). After initial pressurization, an essentially uniform total gas pressure, determined by the preset pressure in the ballast tank, was maintained

between V5 and the manostat. For each experiment the flow was maintained for at least twice the time to replace the gas in the tube, and then stopped by simultaneously closing valves V1 and V2.

walls on the experimental results. The possible occurrence of adsorption between the time the flow was stopped and the shock fired was investigated by withdrawing samples for analysis from a typical, unshocked gas mixture at various

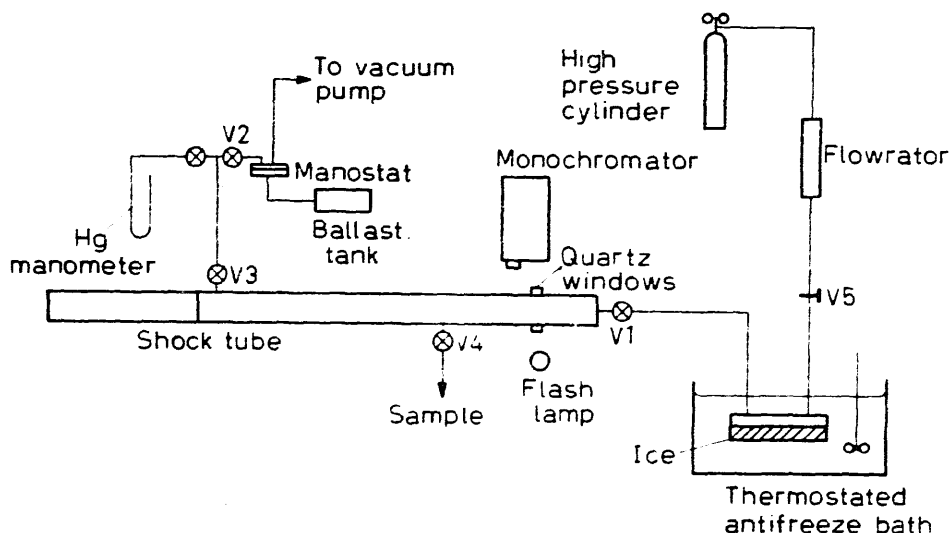


FIGURE 1. Schematic of flow-fill apparatus and shock tube

The partial pressure, and hence mole fraction, of water vapour in these gas mixtures was determined by analysing samples withdrawn through valve V4. The water vapour was condensed from the samples and the pressures of both the remaining mixture and the re-evaporated water were measured manometrically. Analysis of a number of samples taken for each of the three antifreeze bath temperatures used in this investigation yielded mean partial pressures of 2.3, 3.3 and 3.4 mm Hg. These values, which were used in the calculation of the compositions of the initial unshocked gas mixtures, were in good agreement with handbook values¹⁵ for the vapour pressure of ice at the bath temperature indicating that the various gas mixtures became saturated with water vapour while flowing over the ice. This was further confirmed in one test in which a factor-of-two reduction in the flowrate did not affect the measured partial pressure.

Tests were performed to assess the influence of adsorption of water vapour by the shock tube

times after the end of the usual flow period. No change in the measured partial pressure of water vapour was observed over a period of 75 minutes. In another test the flow was stopped in the usual manner and the entire volume between V1 and V3 was slowly pumped down to less than $1\mu\text{m}$ through a liquid nitrogen trap in an attempt to measure the amount of water adsorbed on the shock tube walls during a typical experiment. The analysis showed that only about two per cent of the total water recovered came from the shock tube walls. It is doubtful if this small amount could have influenced recombination in any significant way even if it had been stripped from the walls following the passage of the shock wave.

Experimental hydrogen-oxygen-argon-water vapour mixtures prepared with the flow-fill apparatus are listed in Table 1, where column 6 is the initial H_2/O_2 ratio of these mixtures. The meaning of column 7 will be explained shortly. For comparison, recombination data were also taken under carefully matched conditions in

TABLE 1. Experimental hydrogen-oxygen-argon-water vapour mixtures

Mixture	Initial composition, %				$\frac{H_2}{O_2 _0}$	$\frac{H_2}{O_2 _{eff.}}$
	H ₂	O ₂	Ar	H ₂ O		
A	17.0	1.5	77.5	4.0	11.3	6.0
B	11.0	1.0	85.6	2.4	11.0	6.1
C	5.5	1.0	88.4	5.1	5.5	3.0
D	4.2	1.0	92.2	2.6	4.2	3.0
E	3.0	1.0	89.9	6.1	3.0	2.25
F	1.0	3.0	92.0	4.0	0.33	1.0
G	1.0	10.1	81.0	7.9	0.099	0.63
H	1.0	10.5	84.3	4.2	0.095	0.41

hydrogen-oxygen-argon mixtures with compositions: 1.0% H₂-3.0% O₂-96.0% Ar, 2.25% H₂-0.75% O₂-97.0% Ar, and 6.0% H₂-1.0% O₂-93.0% Ar. Temperatures and pressures for all of these experiments were between 1259° and 1862°K, and 1.1 and 3.7 atm.

All of the experiments described in the preceding paragraph were performed after significant changes had been made in the water vapour source lamp. The modification became necessary when deterioration of the lamp electrodes resulted in a sudden increase in the frequency of anomalous intensity/time emission profiles. The lamp was thoroughly cleaned, filled with fresh sodium acetate (NaC₂H₃O₂·3H₂O) and anhydrous NaC₂H₃O₂, and sealed as before¹⁶. The resulting emission profile was nearly identical to that observed under satisfactory conditions previously. No anomalous behaviour was observed.

However, it became obvious in the first experiments performed after this change that the absorption by OH in H₂/O₂ = 0.33 mixtures was significantly larger than observed previously under identical shock tube experimental conditions. These larger absorbances, when converted into OH concentrations, [OH], with the calibration of Bird and Schott¹⁶ yielded values of [OH] that were unrealistically large. This result was not affected by recleaning and re-sealing the source lamp. We are forced to conclude that a fundamental change in the emission spectrum of the lamp has invalidated the calibration.

It was thus necessary to study in more detail

the new calibration relationship between absorbance ($-\log_{10}$ of the fractional transmission) and [OH] for the same spectral region used previously¹⁶. Low density experiments were carried out in hydrogen-oxygen-argon mixtures with initial H₂/O₂ ratios of 6.0, 3.0 and 0.33 and percentages of reactants between 2.0 and 15.0 at the temperatures of interest in the recombination experiments. At these low densities, recombination—a three body process—is greatly inhibited, and the peak absorbance is

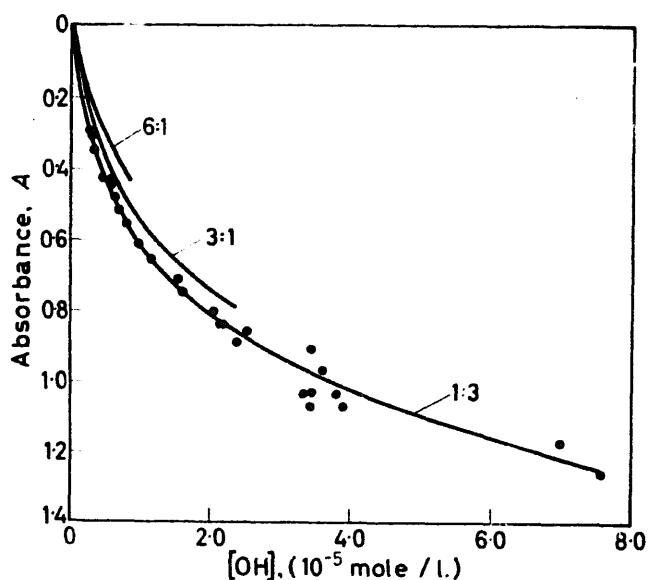


FIGURE 2. Calibration curves for hydrogen/oxygen ratios of 6.0, 3.0 and 0.33. Curves show range in [OH] investigated. Temperature and pressure ranges: 6:1—1548° to 1803°K and 0.21 to 0.95 atm; 3:1—1375° to 1895°K and 0.15 to 1.5 atm; and 0.33—1289° to 1538°K and 0.20 to 3.4 atm

essentially that of the OH concentration computed for partial equilibrium without any recombination.

Curves representing polynomial fits of peak absorbance versus computed [OH] for these mixtures are shown in Figure 2. All of the data for the $H_2/O_2 = 0.33$ experiments are shown in order to illustrate the scatter inherent in this type of experiment. Full ranges in both temperature and total pressure covered in these experiments are given in the caption. No systematic deviation from these curves was observed over these ranges.

It is immediately obvious that the absorbance/[OH] calibration is systematically dependent upon the hydrogen/oxygen ratio. Such a result cannot be accounted for by any convenient extension of the Bird-Schott calibration¹⁶. Accordingly we have proceeded to reduce the absorbance/time data taken in recombination experiments with the modified source lamp to [OH]/time profiles by application in each case of one of these three empirical calibration curves.

A possible complication resulting from this procedure concerns the appropriate curve to use in experiments with added water vapour, since the initial water will affect the reactive species concentrations prevailing during recombination. When water is added, the relative contributions of reactions I to III are determined by an effective H_2/O_2 ratio equal to

$$\left(\frac{H_2}{O_2} \right)_{\text{eff.}} = \frac{(\%H_2)_0 + (\%H_2O)_0}{(\%O_2)_0 + 0.5(\%H_2O)_0} \quad [1]$$

which is given for each mixture in column 7 of Table 1. It was found empirically that the maximum absorbances in the water vapour experiments were interpreted most satisfactorily using $(H_2/O_2)_{\text{eff.}}$ as the parameter correlating the three [OH]/absorbance curves in Figure 2 with the data from the mixtures in Table 1. Accordingly, the 6:1 curve was used for mixtures A and B, the 3:1 curve for mixtures C, D and E, and the 1:3 curve for mixtures F, G and H. A similar, satisfactory correlation was observed using the quantity $(H_2/O_2)_0$ in the three mixtures without added water vapour. It should be noted that use of this procedure for obtaining [OH]/

time profiles yielded rate coefficients that were in satisfactory agreement with those of previous shock tube recombination studies^{2, 7, 8}. This latter point will receive further attention in the Discussion Section.

The driver gas used in all experiments in this investigation was hydrogen at pressures of 9 to 295 lb/in² abs. As in previous shock tube recombination experiments the absence of significant amounts of emission from the shock-heated gases in the spectral region of interest was verified by not firing the source lamp during particular experiments. Periodic mass-spectrographic analyses confirmed the absence of all but trace amounts of impurities in the $H_2-O_2-N_2$ and H_2-O_2-Ar mixtures.

Analysis

As described above a profile of [OH] versus laboratory time, τ , was derived from each recombination experiment. Following the procedure outlined in previous papers^{2, 8} we have combined this information with the assumption that recombination proceeds through a series of partial equilibrium states to compute time-variation profiles for the other significant species in the system and for v , a non-dimensional progress variable, which decreases from 1 to 0 as recombination proceeds.

$$v = (N - N_{\text{eq.}})/(1 - N_{\text{eq.}}) \quad [2]$$

Here N is the number of moles in the system at any instant per initial mole, and $N_{\text{eq.}}$ is its value at full equilibrium.

At this point we assume the mechanism of recombination under these experimental conditions to have been satisfactorily established in previous papers as consisting of only reactions I-III. Accordingly, equation 1 of ref. 2, which describes recombination during any particular experiment, can be simplified to the form

$$\begin{aligned} R_{\text{rec.}} &= - \frac{p_0}{RT_0} (1 - N_{\text{eq.}}) \frac{dv}{d\tau} \\ &= k_{\text{I}}^{\text{eff.}} [H]^2 [X] + k_{\text{II}}^{\text{eff.}} [H] [O_2] [X] \\ &\quad + k_{\text{III}}^{\text{eff.}} [H] [OH] [X] \end{aligned} \quad [3]$$

where $R_{\text{rec.}}$ is the total rate of recombination in units of moles disappearing per cm³-sec, p_0 and T_0 are the initial pressure and temperature,

$[X]$ is the instantaneous concentration of the inert argon or nitrogen, and the effective rate coefficient for reaction j , $k_j^{\text{eff.}}$, is defined by

$$k_j^{\text{eff.}} = \frac{1}{[X]} \sum_{i=1}^7 k_j^{M_i} [M_i] \quad [4]$$

Previous investigations have also shown that equation 3 can be further simplified for recombination in lean or rich mixtures. In mixtures with a significant excess of oxygen, reaction II becomes the dominant path leading to complete equilibrium and

$$-\frac{p_0}{RT_0} (1 - N_{\text{eq}}) \frac{dv}{d\tau} = k_{\text{II}}^{\text{eff.}} [H] [O_2] [X] \quad [5]$$

In the presence of significant amounts of unreacted hydrogen, reaction II is unimportant and $[OH]$ and $[H]$ remain nearly proportional to one another as recombination proceeds. Equation 3 then becomes

$$-\frac{p_0}{RT_0} (1 - N_{\text{eq}}) \frac{dv}{d\tau} = k_{\text{app.}} [H]^2 [X] \quad [6]$$

where the apparent coefficient $k_{\text{app.}}$ is defined by

$$k_{\text{app.}} = k_{\text{I}}^{\text{eff.}} + \alpha k_{\text{III}}^{\text{eff.}} \quad [7]$$

and

$$\alpha = [OH]/[H] \quad [8]$$

In near-stoichiometric mixtures all three reactions, I-III, play an important role in recombination.

The three equations, 3, 5 and 6, have been combined with the results of computations of concentrations and v values to yield values of the effective coefficients $k_{\text{I}}^{\text{eff.}}$ to $k_{\text{III}}^{\text{eff.}}$ as a function of experimental conditions. This information in turn has been combined with equation 4 to determine, as completely as possible, the elementary rate coefficients of interest. These elementary coefficients have been assumed in the analysis to be independent of temperature for the range of temperatures of our experiments.

Instantaneous values of the slope $dv/d\tau$ for these calculations were obtained by using a least squares fitting procedure to relate $\ln v$ and $\ln \tau$ for each experiment in a quadratic expression, and then differentiating at v values where $[OH]$ is known⁸. One solution of the appropriate equation, 3, 5 or 6, was taken as a representative result for each experiment. The v value at which this computation was carried out was chosen from the region where $dv/d\tau$ was best determined.

Results

Recombination in nitrogen mixtures

Equation 5 was used to treat the reduced data from experiments carried out in the 1.0% H_2 -3.0% O_2 -96.0% N_2 mixture. The validity of this equation was tested by verifying the first order relationship between $-dv/d\tau$ and $[H]$ predicted for recombination in a highly dilute, lean mixture. Table 2 summarizes the results of this series of experiments. \bar{T} is the mean reaction zone temperature, $(T_{v=1} + T_{v=0})/2$, and v the value of the progress variable at which $k_{\text{II}}^{\text{eff.}}$ in column 4 was computed. $k_{\text{II}}^{\text{eff.}}$ is essentially

TABLE 2. Summary of recombination results in 1.0% H_2 -3.0% O_2 -96.0% N_2 mixture*

\bar{T} (calc)	p_0 (obs)	$v \times 10^2$ (calc)	$k_{\text{II}}^{\text{eff.}} \times 10^{-14}$	$[H_2O]/[N_2] \times 10^2$	$k_{\text{II}}^{N_2} \times 10^{-14}$
1306	9.81	4.1	29.3	1.0	25.0
1325	9.81	3.9	23.7	1.0	19.4
1327	9.80	5.1	27.5	1.0	23.2
1334	9.80	4.0	25.0	1.0	20.7
1467	7.60	5.1	30.5	1.0	26.2
1492	7.62	4.8	24.2	1.0	19.9
1497	7.62	5.1	22.8	1.0	18.5
1594	6.02	8.8	22.9	1.0	18.6
1603	5.98	7.6	21.9	1.0	17.6
1612	6.02	7.5	23.3	1.0	19.0

* Temperatures are in degrees Kelvin, pressures in centimetres of mercury, and $k_{\text{II}}^{\text{eff.}}$ and $k_{\text{II}}^{N_2}$ in $(\text{cm}^6)/\text{mole}^2$ seconds.

independent of ν . A comparison of the tabulated values of $k_{II}^{eff.}$ with those listed for mixture A-2 in Table 3 of ref. 8 shows that recombination in this nitrogen mixture is only slightly faster than in a similar argon mixture.

Further analysis of these lean results involves the use of equation 4. At the ν values listed in Table 2 the only species with concentrations large enough to permit significant participation as third bodies in reaction II are N_2 , H_2O and O_2 . Thus with some rearrangement equation 4 becomes

$$k_{II}^{eff.} = k_{II}^{N_2} + \frac{[H_2O]}{[N_2]} \left(k_{II}^{H_2O} + k_{II}^{O_2} \frac{[O_2]}{[H_2O]} \right) = k_{II}^{N_2} + \beta [H_2O]/[N_2] \quad [9]$$

where β is equal to

$$k_{II}^{H_2O} + k_{II}^{O_2} \frac{[O_2]}{[H_2O]}$$

In work with argon⁸ it was found that for 1% H_2 -3% O_2 mixtures $\beta \approx k_{II}^{H_2O}$ or $4.3 \times 10^{16} \text{ cm}^6/\text{mole}^2 \text{ sec}$. Thus equation 9 can be used to obtain values of $k_{II}^{N_2}$ from the tabulated effective coefficients $k_{II}^{eff.}$. The last column in Table 2 shows the result of this computation. These values of $k_{II}^{N_2}$ can best be represented by the average value of $2.1 \times 10^{15} \text{ cm}^6/\text{mole}^2 \text{ sec}$ at a mean temperature of approximately 1500°K.

Values of the elementary rate coefficients $k_I^{N_2}$ and $k_{III}^{N_2}$ can be obtained by combining data from experiments in the other two H_2 - O_2 - N_2 mixtures with the results just described. A representative value of $k_{app.}$ is first computed for each experiment in the rich and near-stoichiometric mixtures. Equations 7 and 4 can then be used to obtain the desired coefficients.

In experiments in the 6.0% H_2 -1.0% O_2 -93.0% N_2 (6:1) mixture contributions by reaction II to recombination are negligible, and equation 6 has been used to compute $k_{app.}$. The contribution of reaction II to recombination in the 1.65% H_2 -0.75% O_2 -97.6% N_2 (2.2:1) mixture amounts to approximately 25 per cent of the total rate, and must be taken into consideration before values of $k_{app.}$ can be obtained. Accordingly, equation 3 has been rearranged to the form

$$-\frac{p_0}{RT_0} (1 - N_{eq.}) \frac{d\nu}{d\tau} - k_{II}^{eff.} [H] [O_2] [N_2] = k_{app.} [H]^2 [N_2] \quad [10]$$

which permits values of $k_{app.}$ to be computed after subtraction of the rate of reaction II from the total recombination rate. For these calculations $k_{II}^{eff.}$ was taken as

$$k_{II}^{N_2} + k_{II}^{H_2O} \frac{[H_2O]}{[N_2]}$$

evaluated from the lean mixture results above. These computations of $k_{app.}$ were for a ν of 0.21 to 0.36 and reaction zone temperatures near 1600°K. Figure 3 is a graph of the computed values of $k_{app.}$ against α following equation 7. The larger values of α correspond to experiments in the 2.2:1 mixture.

These values of $k_{app.}$ can be compared directly with apparent coefficients obtained at comparable α s in argon mixtures. Argon data are available from previous investigations^{2,7}, and from eleven experiments carried out in the 6.0% H_2 -1.0% O_2 -93.0% Ar mixture and analysed with equation 6. A comparison shows that, as in the 1:3 mixtures, the rate of recombination in

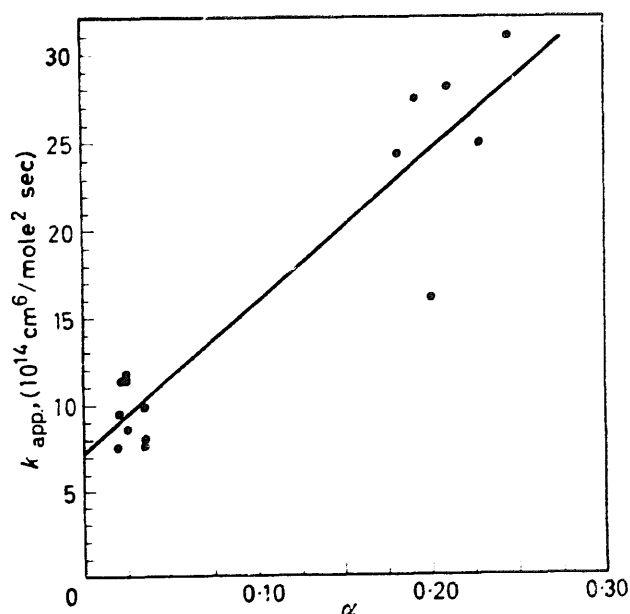


FIGURE 3. $k_{app.}$ versus α for nitrogen experiments in 2.2:1 and 6:1 mixtures at 1518° to 1912°K. Position of line determined by least-squares fit

rich mixtures is slightly enhanced by the substitution of nitrogen for argon as the diluent.

For the intercept and slopes of the least-squares straight line in Figure 3 to be interpretable in terms of elementary rate coefficients it is necessary that in the two experimental mixtures contributions of third bodies other than nitrogen to $k_1^{\text{eff.}}$ and $k_{\text{III}}^{\text{eff.}}$ be small in comparison with those of the inert (see equation 4). Otherwise $k_1^{\text{eff.}}$ and $k_{\text{III}}^{\text{eff.}}$ will be functions of α . The near-equality of the intercept $k_1^{\text{eff.}} = 7.1 \times 10^{14} \text{ cm}^6/\text{mole}^2 \text{ sec}$, and $k_1^{\text{N}_2}$, and of the slope $k_{\text{III}}^{\text{eff.}} = 8.6 \times 10^{15} \text{ cm}^6/\text{mole}^2 \text{ sec}$, and $k_{\text{III}}^{\text{N}_2}$, are assured by high dilution with nitrogen in these mixtures.

A reasonable estimate of the small difference between $k_1^{\text{eff.}}$ and $k_1^{\text{N}_2}$ has been made by using rate coefficients available in the literature. Since at the v values at which the computations of $k_{\text{app.}}$ were performed the only important third bodies are N_2 , H_2O and H_2 , equation 4 can be simplified to the form

$$k_1^{\text{eff.}} = k_1^{\text{N}_2} + k_1^{\text{H}_2\text{O}} \frac{[\text{H}_2\text{O}]}{[\text{N}_2]} + k_1^{\text{H}_2} \frac{[\text{H}_2]}{[\text{N}_2]} \quad [11]$$

For this computation $k_1^{\text{H}_2\text{O}}$ was taken⁷ as $2.0 \times 10^{15} \text{ cm}^6/\text{mole}^2 \text{ sec}$ and $k_1^{\text{H}_2}$ as $2.5 \times 10^{18}/T$ (ref. 13) ($= 1.6 \times 10^{15} \text{ cm}^6/\text{mole}^2 \text{ sec}$ at 1600°K). In the 6:1 mixture the computed contributions of H_2 and H_2O amount to some 15 per cent of $k_1^{\text{eff.}}$, and a value of $k_1^{\text{N}_2} = 6.0 \times 10^{14} \text{ cm}^6/\text{mole}^2 \text{ sec}$ is obtained. In view of the uncertainties involved, we have chosen not to apply a similar correction to $k_{\text{III}}^{\text{eff.}}$. $k_{\text{III}}^{\text{N}_2}$ was taken as approximately equal to $k_{\text{III}}^{\text{eff.}}$.

All three of the nitrogen coefficients are entered in Table 3 for comparison, where possible, with other determinations.

Recombination in water vapour experiments

Contrary to the method of minimizing contributions to recombination of third bodies other than argon or nitrogen used in previous shock tube studies, the water vapour experiments were carried out with the objective of enhancing the contribution of H_2O to the point where the coefficients $k_1^{\text{H}_2\text{O}}$ to $k_{\text{III}}^{\text{H}_2\text{O}}$ could be measured reliably. To accomplish this it was necessary to introduce into the reaction zone following the shock wave percentages of H_2O that were considerably larger than those of previous

experiments. The flow-fill method was chosen for this purpose because it allows the introduction of significant, well-determined quantities of water vapour into the shock tube, while avoiding the adverse effects associated with the exothermicity of hydrogen-oxygen mixtures containing large percentages of reactants.

Unfortunately, since it is necessary to study recombination in mixtures containing effective H_2/O_2 ratios far from the stoichiometric ratio of two, the use of larger percentages of H_2O requires correspondingly larger percentages of H_2 or O_2 in the reacting mixtures (see equation 1). This in turn greatly complicates the analysis of third body effects, particularly in rich mixtures. In lean mixtures, as will be seen, $k_{\text{II}}^{\text{H}_2\text{O}}$ is much greater than $k_{\text{II}}^{\text{O}_2}$ and the contribution of O_2 to $k_{\text{II}}^{\text{eff.}}$ can be ignored.

Another complication was introduced into the analysis by the necessity of having to use a 'different' source lamp and calibration for the water vapour experiments. Results obtained with this lamp* in selected hydrogen-oxygen-argon mixtures differed somewhat from those previously obtained under similar conditions with Lamp I. For example, although recombination in a 1.0% H_2 -3.0% O_2 -96.0% Ar mixture is characterized in both cases by a clear first order relationship between $-dv/d\tau$ and $[\text{H}]$, computed values of $k_{\text{II}}^{\text{eff.}}$ in experiments with Lamp II average about 50 per cent higher than in the original experiments ($3.0 \times 10^{15} \text{ cm}^6/\text{mole}^2 \text{ sec}$ versus $1.9 \times 10^{15} \text{ cm}^6/\text{mole}^2 \text{ sec}$). The agreement between computed values of $k_{\text{app.}}$ in a 6.0% H_2 -1.0% O_2 -93.0% Ar mixture is somewhat better ($12.3 \times 10^{14} \text{ cm}^6/\text{mole}^2 \text{ sec}$ versus $9.0 \times 10^{14} \text{ cm}^6/\text{mole}^2 \text{ sec}$). Further attention will be given to these differences in the Discussion section. In this attempt to determine the three termolecular coefficients for $M = \text{H}_2\text{O}$ we have restricted our attention to experiments carried out with Lamp II.

Recombination in the lean water vapour mixtures F-H and in the standard 1.0% H_2 -3.0% O_2 -96.0% Ar mixture will be examined first. The validity of equation 5 for the analysis of

* Hereafter this second water vapour source lamp, with its empirical calibration curves, will be referred to as Lamp II. The original lamp and its semi-empirical calibration will be denoted by Lamp I.

the reduced data from these experiments was established by verifying the predicted linear relationship between $-dv/d\tau$ and $[H]$. A logarithmic plot of these two quantities is shown in Figure 4 for three experiments in mixture F

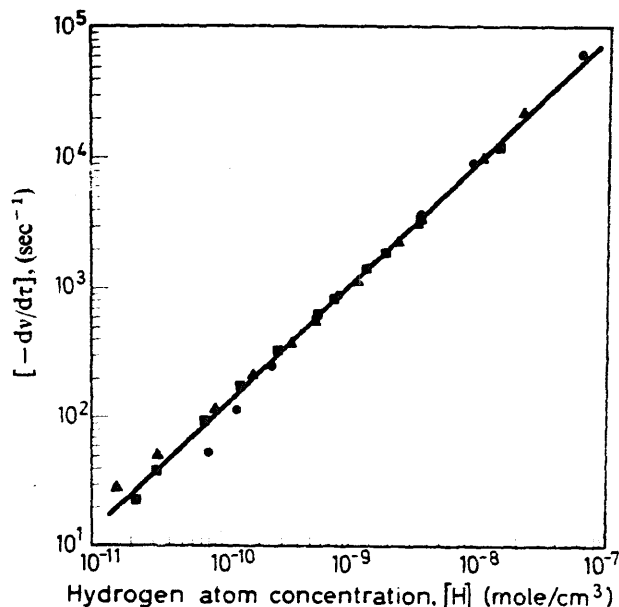


FIGURE 4. Dependence of recombination rate on hydrogen atom concentration for mixture F. Results of three experiments with $p_0 = 8.2$ cm Hg and $T \sim 1510$ K are denoted by symbols ●, ■, and ▲. v values are between 1.0 and 0.008 and cover a period of about 500 μ sec. Slope of line determined by least-squares fit = 0.96 ± 0.01

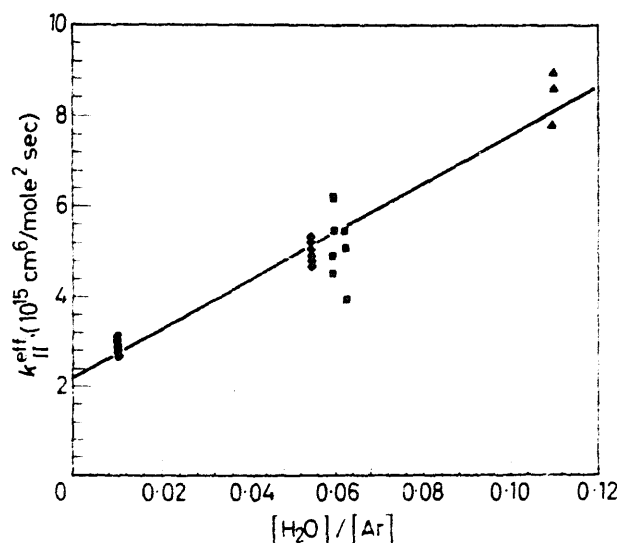


FIGURE 5. k_{II}^{eff} versus $[H_2O]/[Ar]$ for 22 experiments in lean water vapour mixtures at 1259° to 1550° K. ● $[O_2]/[H_2O] = 2.5$; ■ $[O_2]/[H_2O] = 2.0$; ▲ $[O_2]/[H_2O] = 1.0$; and ◆ $[O_2]/[H_2O] = 0.5$. Position of line determined by least-squares fit

at approximately 1510°K. A least-squares fit of these points yields a slope of 0.96 ± 0.01 . Graphs of this type have demonstrated that even in mixtures with effective hydrogen/oxygen ratios as large as 1.0 recombination proceeds essentially at the rate of reaction II.

Values of k_{II}^{eff} computed with equation 5 were seen to be essentially independent of v . As in the treatment of the nitrogen data a representative value was chosen from the region where $dv/d\tau$ was best determined, $0.038 \leq v \leq 0.105$. These values of k_{II}^{eff} can be related to the elementary rate coefficients for the third bodies Ar, H_2O and O_2 by equation 9, if the symbol N_2 is replaced by Ar wherever it appears in the equation. Here again we have ignored the contribution to k_{II}^{eff} of species present in very low concentration. β of course is equal to $k_{II}^{H_2O} + k_{II}^{O_2} [O_2]/[H_2O]$, where the ratio $[O_2]/[H_2O]$ is a function of $(H_2/O_2)_{eff}$. A graph of the computed values of k_{II}^{eff} versus the corresponding ratio $[H_2O]/[Ar]$ is shown in Figure 5. In this figure it can be seen that k_{II}^{eff} at $[H_2O]/[Ar] \approx 0.06$ is not significantly affected by a factor of four increase in the ratio $[O_2]/[H_2O]$. The resulting conclusion that $\beta \approx k_{II}^{H_2O}$ is in agreement with previous observations⁸. A least-squares fit of the experimental points in Figure 5 yields a slope, $k_{II}^{H_2O}$, of $5.4 \pm 0.5 \times 10^{16}$ cm⁶/mole² sec and an intercept, k_{II}^{Ar} , of $2.2 \pm 0.3 \times 10^{15}$ cm⁶/mole² sec. By estimating that $k_{II}^{O_2} [O_2]/[H_2O]$ is no larger than 20 per cent of $k_{II}^{H_2O}$ at the largest value of $[O_2]/[H_2O]$, 2.5, we obtain an upper limit on $k_{II}^{O_2}$ of 4.3×10^{15} cm⁶/mole² sec. It should be noted that the introduction of water vapour into the reacting mixtures has made possible rate coefficient measurements at $[H_2O]/[Ar]$ ratios that are nearly a factor of four greater than those utilized previously⁸.

The results of recombination experiments in the six 3:1 and 6:1 mixtures (A-D in Table 1 and the standard mixtures 2.25% H_2 -0.75% O_2 -97.0% Ar and 6.0% H_2 -1.0% O_2 -93.0% Ar) will now be considered. Using the quantities just derived for k_{II}^{Ar} and $k_{II}^{H_2O}$ it can be easily shown that at the v values of interest the contribution of reaction II to the total rate of recombination is negligible in the 6:1 mixtures and amounts to no more than five per cent of the total rate in the 3:1 mixtures. Accordingly, a

representative value of $k_{app.}$ was computed for each experiment using either equation 6—in the cases where no correction for reaction II is required—or equation 10, as modified by the substitution of Ar for N_2 . The apparent coefficients were computed for a v between 0.11 and 0.15.

Reduction of these values of $k_{app.}$ to the elementary rate coefficients is complicated by the fact that two termolecular reactions, and as many as three third bodies, Ar, H_2O and H_2 , play a significant role in determining the recombination rate. In enhancing the importance of water vapour and hydrogen relative to the inert we have made the complexity of the analysis comparable to that encountered in flame studies of recombination.

A useful expression for $k_{app.}$ can be derived by combining equations 4 and 7 in the following manner

$$k_{app.} = k_1^{Ar} + k_1^{H_2O} \frac{[H_2O]}{[Ar]} + k_1^{H_2} \frac{[H_2]}{[Ar]} + \alpha \left(k_{III}^{Ar} + k_{III}^{H_2O} \frac{[H_2O]}{[Ar]} + k_{III}^{H_2} \frac{[H_2]}{[Ar]} \right) \quad [12]$$

and then rearranging to obtain

$$k_{app.} = (k_1^{Ar} + \alpha k_{III}^{Ar}) + \frac{[H_2O]}{[Ar]} \{ \alpha k_{III}^{H_2O} + (k_1^{H_2O} + K_A k_{III}^{H_2}) + \frac{K_A}{\alpha} k_1^{H_2} \} = b + c [H_2O]/[Ar] \quad [13]$$

K_A is the equilibrium constant for the reaction



In addition to being functions of the six termolecular coefficients, b and c in equation 13 are dependent upon the values of α and K_A , which in turn depend upon the composition, i.e. $(H_2/O_2)_{eff.}$ and v , and the temperature. Of course K_A is only a function of temperature. In this investigation b and c have been evaluated in both the 6:1 and 3:1 mixtures by observing the dependence of $k_{app.}$ on the ratio $[H_2O]/[Ar]$ for nearly constant v and temperature values that were the same in both mixtures. Thus in all these experiments K_A is approximately a con-

stant and α depends only on $(H_2/O_2)_{eff.}$ b and c are then constants for a given $(H_2/O_2)_{eff.}$ The two sets of b and c values have been combined to yield further information about the termolecular coefficients.

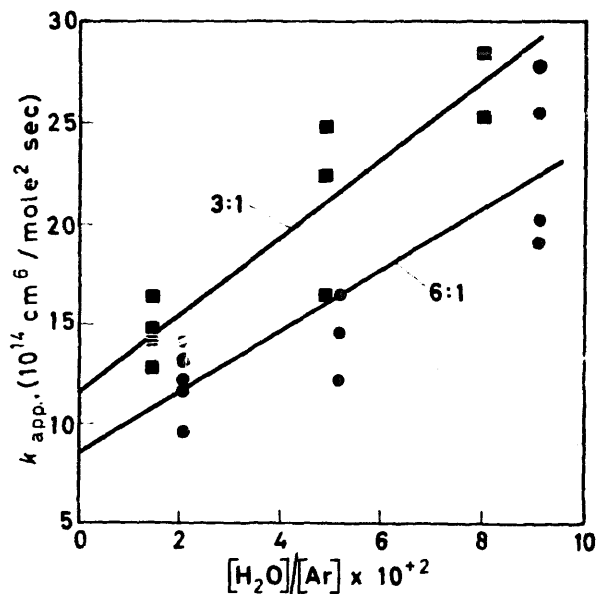


FIGURE 6. Dependence of $k_{app.}$ on $[H_2O]/[Ar]$ for 6:1 and 3:1 water vapour mixtures. ● 6:1 experiments: $1641^\circ \leq T \leq 1768^\circ K$. ■ 3:1 experiments: $1633^\circ \leq T \leq 1711^\circ K$. Least-squares slopes and intercepts in units of $10^{16} \text{ cm}^6/\text{mole}^2 \text{ sec}$: 6:1— 1.50 ± 0.26 and 0.86 ± 0.15 ; and 3:1— 1.90 ± 0.28 and 1.16 ± 0.12

Figure 6 is a graph of $k_{app.}$ versus $[H_2O]/[Ar]$ for results in both the 6:1 and 3:1 mixtures. For reasons stated above only those experiments with $0.029 \leq \alpha \leq 0.038$ and $0.057 \leq K_A \leq 0.073$ ($1715 \leq T_v \leq 1825^\circ K$) in the 6:1 mixtures, and $0.11 \leq \alpha \leq 0.14$ and $0.053 \leq K_A \leq 0.065$ ($1690 \leq T_v \leq 1765^\circ K$) in the 3:1 mixtures are included on this graph. Most of the actual experiments fell within these ranges, which were chosen so that the small variation of b and c with α and K_A could be ignored.

Least squares fits of the experimental points in Figure 6 yield: $b_{6:1} = 8.6 \times 10^{14}$, $c_{6:1} = 1.50 \times 10^{16}$, $b_{3:1} = 11.6 \times 10^{14}$; and $c_{3:1} = 1.90 \times 10^{16}$, in units of $\text{cm}^6/\text{mole}^2 \text{ sec}$. Since $b = k_1^{Ar} + \alpha k_{III}^{Ar}$, combination of the two values of b at mean α s (0.033 and 0.125) results in the solution: $k_1^{Ar} = 7.5 \times 10^{14} \text{ cm}^6/\text{mole}^2 \text{ sec}$ and $k_{III}^{Ar} = 3.3 \times 10^{15} \text{ cm}^6/\text{mole}^2 \text{ sec}$.

The data at hand are insufficient to separate the four coefficients in the expression for the slope, c , without additional assumptions. Note that the expression for c is of the form $\alpha d + e + f/\alpha$, where d , e and f are constants in these experiments. As a first assumption we accept the expression of Jacobs *et al.*¹³ for $k_1^{\text{H}_2}$, which at higher temperatures is in quite satisfactory agreement with the results of other hydrogen dissociation measurements. Extrapolated to 1700°K this expression yields $1.5 \times 10^{15} \text{ cm}^6/\text{mole}^2 \text{ sec}$. With this value the quantity f/α , $(K_A/\alpha) k_1^{\text{H}_2}$, can be computed for each mixture and then subtracted from the corresponding values of c to obtain the quantity c' , which is equal to $\alpha d + e$. Combination of these two values of c' with the corresponding mean values of α yields the solution: $d = k_{\text{III}}^{\text{H}_2\text{O}} = 6.6 \times 10^{16} \text{ cm}^6/\text{mole}^2 \text{ sec}$ and $e = k_1^{\text{H}_2\text{O}} + K_A k_{\text{III}}^{\text{H}_2} = 1.0 \times 10^{16} \text{ cm}^6/\text{mole}^2 \text{ sec}$. The quantity $(c - c')/c$ was not large, 0.19 in the 6:1 mixtures and 0.04 in the 3:1 mixtures; thus small errors in $k_1^{\text{H}_2}$ would not significantly affect the resulting values of d and e .

Separation of the coefficients $k_1^{\text{H}_2\text{O}}$ and $k_{\text{III}}^{\text{H}_2}$ is more difficult. The relative rates of reaction I with $M = \text{H}_2\text{O}$ and reaction III with $M = \text{H}_2$ are of course related by the equilibrium IV and can only be changed by varying the temperature. Because of the uncertainties encountered in developing the empirical calibration curve and

the fact that the term involving e in equation 13 is always less than $0.5 k_{\text{app}}$, even at the maximum $[\text{H}_2\text{O}]/[\text{Ar}]$ ratio in either mixture, no attempt was made to separate these two coefficients. Upper limits were assigned as follows: $k_1^{\text{H}_2\text{O}} \leq e$ and $k_{\text{III}}^{\text{H}_2} \leq e/K_A$, where K_A was taken as 0.063.

All of the elementary termolecular coefficients obtained from the water vapour experiments are listed in Table 3.

It should be noted that experimental data taken in six experiments at temperatures between 1528° and 1622°K in mixture E $[(\text{H}_2/\text{O}_2)_{\text{eff.}} = 2.25]$ provide an opportunity to test the accuracy of these coefficients. Although a calibration curve for absorbance versus $[\text{OH}]$ was not determined for this particular H_2/O_2 ratio, the analysis was carried out with the curve for 3:1 mixtures, which is likely to be very close to being correct at the low hydroxyl radical concentrations ($< 1 \times 10^{-5} \text{ moles/l.}$) of interest. In this manner experimental values of the total recombination rate, i.e. the LHS of equation 3, have been computed at points where recombination is between 73 and 81 per cent complete. The Lamp II coefficients listed in Table 3 have been combined with the partial equilibrium concentrations and values of α and K_A in an attempt to predict each experimental $R_{\text{rec.}}$ by evaluating the RHS of equation 3. All three reactions contribute significantly to recombination under these conditions. The agreement

TABLE 3. Summary of pertinent rate coefficient values^(a)

Reaction	M					$k_j^{\text{N}_2}/k_j^{\text{Ar}}$	$k_j^{\text{H}_2\text{O}}/k_j^{\text{Ar}}$
	Ar	N ₂	H ₂ O	H ₂	O ₂		
I	4 ^(b)	6 ^(c)	—	—	—	1.5	—
I	7.5 ^(d)	—	≤ 100 ^(d)	15 ^(e)	—	—	≤ 13
I	—	5.4 ^(f)	≤ 36 ^(f)	86 ^(f)	—	—	—
I	—	8.5 ^(h)	8.5 ^(h)	55 ^(h)	—	—	—
II	14 ^(b)	21 ^(c)	430 ^(b)	—	—	1.5	30
II	22 ^(d)	—	540 ^(d)	—	≤ 43 ^(d)	—	25
II	33 ⁽ⁱ⁾	—	—	—	—	—	—
III	54 ^(b)	86 ^(c)	—	—	—	1.6	—
III	33 ^(d)	—	660 ^(d)	≤ 1600 ^(d)	—	—	20
III	—	470 ^(g)	1020 ^(g)	≤ 3630 ^(g)	—	—	—
III	—	550 ^(h)	550 ^(h)	—	—	—	—

(a) All coefficients in units of $10^{14} \text{ cm}^6/\text{mole}^2 \text{ sec}$; (b) previous work with Lamp I; (c) this work—Lamp I; (d) this work—Lamp II; (e) from ref. 13 extrapolated to 1700°K; (f) from ref. 4 at 1400°K, converted to present units and definitions by multiplication by $(N_A/2)$, where N_A is Avogadro's number; (g) from ref. 4 at 1400°K converted by multiplication by $N_A/2$; (h) from ref. 3 at 1072 K, converted by division by two; (i) from ref. 24 at 1100°K.

between experimental and predicted recombination rates is found to be quite satisfactory. The average absolute deviation of the predicted from the experimental rates is only 17 per cent and there were no systematic differences between the two rates.

Discussion and Conclusions

In the reduction of absorption data taken in the nitrogen experiments to $[\text{OH}]/\text{time}$ profiles use was made of a slightly larger value for the pressure broadening parameter, a , than the one found appropriate for argon mixtures. The difference in the two expressions for a , $350 \bar{p}/\bar{T}$ and $285 \bar{p}/\bar{T}$, is essentially a measure of the relative effectiveness of nitrogen and argon in broadening the important OH absorption lines. Recent data¹⁷ on the room temperature pressure broadening of OH ultra-violet absorption lines indicate that the difference between the two inert gases is slight, with nitrogen being a somewhat more effective broadening agent. Estimates based on the limited quantitative data available indicate that a ratio $a_{\text{N}_2}/a_{\text{Ar}}$ of $350/285 = 1.23$ is reasonable. In any case, however, the influence of pressure broadening at the temperatures and pressures of these shock tube experiments is very small. The effect of this variation in a has been shown to be insignificant in comparison with the scatter in the experimental results.

Implicit in the analysis of the nitrogen data were the assumptions that N_2 is both vibrationally relaxed and chemically inert throughout the recombination portion of the reaction zone. It is believed that in an atmosphere containing one per cent or more water vapour vibrational relaxation of N_2 will be essentially complete before any significant amount of recombination has occurred. Recent evidence indicates that the reactants H_2 ¹⁸ and O_2 ^{19, 20} and oxygen atoms²⁰ will also catalyse the attainment of thermal equilibrium in nitrogen. It can be shown that at these temperatures chemical reactions involving nitrogen²¹ are too slow to have influenced our results.

The treatment of absorption data taken in the water vapour experiments was complicated considerably by the difficulties encountered with the light source. Attempts to explain the larger absorbances and strong dependence upon the

hydrogen/oxygen ratio observed in the Lamp II absorption data within the framework of the Lamp I calibration were unsuccessful. A lower level of background continuum in the lamp cannot by itself account for the observed composition dependence. A combination of a lower continuum emission and pressure broadening by some constituent of the experimental gas mixtures has been ruled out on the basis of computations using the Bird-Schott computer code¹⁶ and the incompatibility of the experimental observations with the assumption of broadening by any of the species present. This conclusion is in agreement with results reported by Kaskan²² on pressure broadening of OH absorption lines in various flame gas mixtures. At this point, rather than attempt a detailed re-examination of the emission characteristics of the flash lamp, we chose to treat the recombination data by making use of the three empirical calibration curves.

Considerable justification for the essential correctness of this procedure is provided by the agreement of these results with those of previous shock tube studies in argon. The earlier conclusion² that the mechanism of recombination for a wide range of initial hydrogen/oxygen ratios consists of only reactions I to III has been confirmed. Values for the four rate coefficients $k_{\text{I}}^{\text{Ar}}-k_{\text{III}}^{\text{Ar}}$ and $k_{\text{II}}^{\text{H}_2\text{O}}$ have been obtained that are in reasonable agreement with earlier determinations (see Table 3). In this comparison it should be recalled that $k_{\text{III}}^{\text{Ar}}$ for Lamp I is somewhat larger than the true value because it is really $k_{\text{III}}^{\text{eff}}$, uncorrected for the previously unknown contributions of other third bodies². The differences between these two sets of coefficients most likely result from differences in the accuracy of the two calibrations, and are an indication of the uncertainties in the tabulated values. The sensitivity of these coefficients to the calibration is greatest in lean mixtures where the total rate of recombination is proportional to the cube of the OH concentration⁸.

Of particular significance among the results for Lamps I and II listed in Table 3 are the ratios of the rate coefficients $k_{\text{I}}^{\text{N}_2}/k_{\text{I}}^{\text{Ar}}$ and $k_{\text{I}}^{\text{H}_2\text{O}}/k_{\text{I}}^{\text{Ar}}$ listed in the last two columns. These numbers are least dependent upon the calibration uncertainties. It is particularly interesting to note that in

all three reactions the ratio of the nitrogen coefficient to that of argon is approximately 1.5. Both the ratios $k_{\text{II}}^{\text{N}_2}/k_{\text{II}}^{\text{Ar}}$ and $k_{\text{II}}^{\text{H}_2\text{O}}/k_{\text{II}}^{\text{Ar}}$, 1.5 and 30 or 25, are in close agreement with the corresponding ratios determined from second explosion limit conditions²³.

Also listed in Table 3 for comparison are rate coefficients determined in several recent shock^{13,24} and flame studies^{3,4} carried out at temperatures similar to those of the present work. The extrapolated value $k_{\text{I}}^{\text{H}_2}$ of Jacobs *et al.*¹³ is included because it was used in our analysis. The other shock tube value is that of Gutman *et al.*²⁴ who observed the effect of reaction II on the rate of chain branching in dilute hydrogen-oxygen-argon mixtures at somewhat lower temperatures. The agreement with our most recent value is not bad if account is taken of the small, negative activation energy of the rate coefficient.

As mentioned earlier the flame studies suffer from the same disadvantage as our rich water vapour experiments, namely significant participation by at least three important third bodies in each of two recombination reactions. In the flame investigations this problem affects the accuracy of the determination of all six elementary rate coefficients. For this reason it is believed that our nitrogen coefficients, which were determined in separate experiments using very high dilution with the inert, are more reliable than the flame values. Indeed, attempts to predict experimental values of k_{app} , observed in our 6:1 and 2.2:1 nitrogen experiments using the flame coefficients in equations 4 and 7 have yielded computed apparent coefficients that are a factor of two to four too large. This result can be traced directly to the large values of $k_{\text{III}}^{\text{N}_2}$ reported in refs. 3 and 4, which cause the term involving this coefficient to dominate the expression for k_{app} , even in the 6:1 mixtures.

The accuracy of our set of elementary coefficients has been tested by attempting to predict the experimental flame values of k_a ³ and kM ⁴. Coefficients obtained from the water vapour experiments were combined with the ratios $k_{\text{I}}^{\text{N}_2}/k_{\text{I}}^{\text{Ar}}$ and $k_{\text{III}}^{\text{N}_2}/k_{\text{III}}^{\text{Ar}}$ in Table 3 and the value $k_{\text{I}}^{\text{H}_2} = 1.5 \times 10^{15} \text{ cm}^6/\text{mole}^2 \text{ sec}$ of Jacobs *et al.*¹³ for this purpose. The predicted values are consistently large by 20 to 50 per cent and

show the correct variation with α . This agreement is not bad, since the predicted values are strongly influenced by the term involving the quantity $k_{\text{I}}^{\text{H}_2\text{O}} + K_A k_{\text{III}}^{\text{H}_2}$, which, because of the dependence of K_A on temperature, might be less than the tabulated value of $1.0 \times 10^{16} \text{ cm}^6/\text{mole}^2 \text{ sec}$ at the lower temperatures of the flame experiments.

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