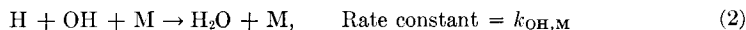
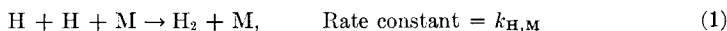


RADICAL RECOMBINATION IN RICH PREMIXED HYDROGEN/OXYGEN FLAMES

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The lithium/lithium hydroxide technique, employing atomic absorption spectroscopy for atomic lithium determination, has been used to study the decay of hydrogen-atom concentrations in fuel-rich, atmospheric-pressure hydrogen/oxygen/diluent flames. The observed second-order rate constants for hydrogen-atom decay are interpreted in terms of the reactions,



where M represents any of the bulk species present in the burnt-gas region of the flame. Analyses of the dependence of the observed second-order rate constant on molecular hydrogen concentration in over one hundred and fifty flames containing as diluent, nitrogen, argon, helium, carbon dioxide or steam have led to the following values (in $\text{ml}^2 \text{ molecule}^{-2} \text{ sec}^{-1}$): $k_{\text{H,N}_2} = 1.0 \times 10^{-32}$, $k_{\text{H,Ar}} = 0.6 \times 10^{-32}$, $k_{\text{H,H}_2\text{O}} = 1.3 \times 10^{-32}$, $k_{\text{OH,N}_2} = 1.3 \times 10^{-32}$, $k_{\text{OH,Ar}} = 1.8 \times 10^{-32}$, $k_{\text{OH,H}_2\text{O}} = 2.0 \times 10^{-32}$, $k_{\text{OH,H}_2\text{O}} = 2.4 \times 10^{-32}$, all at 1900°K. The rate constants $k_{\text{H,H}_2\text{O}}$ and $k_{\text{OH,H}_2\text{O}}$ cannot be determined individually because of the balanced reaction,



and the value $(k_{\text{H,H}_2\text{O}} + Kk_{\text{OH,H}_2\text{O}}) = 2.1 \times 10^{-32} \text{ ml}^2 \text{ molecule}^{-2} \text{ sec}^{-1}$ at 1900°K was obtained.

The algebraic complexity of the rate of recombination in flames diluted with carbon dioxide (when partial reduction to carbon monoxide occurs) prohibits the determination of $k_{\text{H,CO}}$, $k_{\text{H,CO}_2}$, $k_{\text{OH,CO}}$, and $k_{\text{OH,CO}_2}$. A simplified procedure based on the assumption of equal third-body efficiencies for carbon dioxide and carbon monoxide leads to an effective rate constant for Reaction (1) of $1.4 \times 10^{-32} \text{ ml}^2 \text{ molecule}^{-2} \text{ sec}^{-1}$ and an upper limit for the rate constant of Reaction (2) of $0.5 \times 10^{-32} \text{ ml}^2 \text{ molecule}^{-2} \text{ sec}^{-1}$, with these species as third bodies.

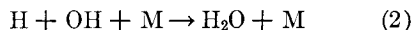
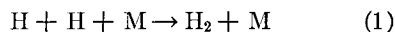
1. Introduction

1.1 Previous Studies of the Subject

Several groups of workers have studied radical recombination rates in the post-reaction zones of laminar flames. The initial study by Bulewicz and Sugden¹ in fuel-rich, hydrogen/oxygen/nitrogen flames at atmospheric pressure was followed by studies in similar systems by Dixon-Lewis, Sutton, and Williams² and by Rosenfeld and Sugden.³ Kaskan carried out work on both fuel-rich⁴ and fuel-lean⁵ low-pressure hydrogen/air flames. McEwan and Phillips⁶ made studies of fuel-lean, atmospheric-pressure hydrogen/oxygen/nitrogen flames, paying particular attention to the agreement with results obtained in near-

stoichiometric flames. Zeegers and Alkemade⁷ made the first study of recombination in near-stoichiometric and fuel-rich acetylene/air flames.

In the simplest of the systems mentioned above there are at least three possible third bodies in each termolecular combination reaction such as (1) or (2),



and it is clear that the total rate of disappearance of radicals is made up of a considerable number of parts. The determination of any single termolecular rate constant must consequently involve the analysis of a substantial number of data.

Attempts to analyze the observed rate data have been made with varying degrees of success but no isothermal separation into individual rate constants has previously been made without assumptions being made about the sizes and/or relative importance of the constants.

A considerable number of studies of recombination reactions at high temperatures have been made in shock tubes. These studies have been concerned mainly with Reaction (1) where M = molecular hydrogen or argon. This work has been discussed in Ref. 8. A shock-tube study of particular interest in connection with the present work was that by Getzinger⁹ which led to a value of the rate constant for Reaction (2) with M = argon.

1.2 Purpose of the Present Work

The aims of the present study were threefold:

(a) to extend the data on recombination reactions of types (1) and (2) to include such third bodies as water, helium, carbon monoxide and carbon dioxide as well as the most frequently studied third bodies, molecular hydrogen, molecular nitrogen, and argon;

(b) to develop a more satisfactory method of analyzing the experimentally observed rate data than has been used by previous workers, based on the use of sets of isothermal flames varying widely in composition, combined with a statistical method of analyzing the data;

(c) to develop an experimental approach based on the established lithium/lithium hydroxide technique,¹⁰ atomic absorption spectroscopy being used for the determination of free atomic lithium concentrations rather than the more usual, but limited, technique of atomic emission spectroscopy.

2. Theoretical

2.1 The Determination of Hydrogen-Atom Concentration

The principles of the lithium/lithium hydroxide technique for the determination of hydrogen-atom concentrations have been described previously^{1,3} and the modification of the method in which atomic absorption spectroscopy is used has been discussed by McEwan and Phillips,¹¹ and by Halstead and Jenkins.¹² In the latter work the relation between reciprocal hydrogen-atom concentration and incident and transmitted intensities (I_0 and I_t , respectively) of lithium resonance radiation is derived:

$$[H]^{-1} = \left(\frac{\theta C_{Li}}{g T^{3/2} F_i \ln(I_0/I_t)} - 1 \right) / K_{Li} [H_2O] \quad (3)$$

where C_{Li} is the concentration of lithium salt (usually the chloride) solution in the atomizer, g is a factor which takes into account the change in volume of the gases on combustion, T is the absolute temperature, F_i is the input (unburned) gas flow-rate, K_{Li} is the equilibrium constant of the balanced Reaction (4)



θ is a constant for a particular flame and is a function of atomizer efficiency, flame composition and temperature and the parameters of the lithium resonance transition at 6707 Å.¹¹

The value of K_{Li} used in the present work is based on the recent work of Jensen and Padley.¹³

2.2 The Kinetics of Radical Recombination in Rich Hydrogen/Oxygen/Diluent Systems

In the post-reaction zones of fuel-rich hydrogen/oxygen flames the rate of recombination is determined by Reactions (1) and (2). Other recombination reactions are unimportant because of the low concentrations of atomic and molecular oxygen.

Thus, to a good approximation, the total rate of disappearance of radicals may be written

$$-d([H] + [OH])/dt = 2[H]^2 \sum_M k_{H,M}[M] + 2[H][OH] \sum_M k_{OH,M}[M] \quad (5)$$

where $k_{H,M}$ and $k_{OH,M}$ represent the rate constants for Reaction (1)

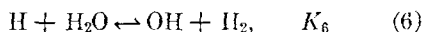
$$-d[H]/dt = 2k_{H,M}[H]^2[M]$$

and Reaction (2)

$$-d[H]/dt = -d[OH]/dt = k_{OH,M}[H][OH][M],$$

respectively, and the summations include all the bulk species present in the burned gases.

With the balanced reaction



and with the relation $[X] = 1 - [H_2] - [H_2O]$, where $[X]$ represents the partial pressure of the diluent gas, Eq. (5) becomes, as first shown by Dixon-Lewis *et al.*,²

$$k_0([H_2] + K_6[H_2O])/2 = A[H_2]^2 + B[H_2] + C \quad (7)$$

where k_0 is the observed recombination rate constant defined by $d[\text{H}]/dt = -k_0[\text{H}]^2$ and

$$A = k_{\text{H},\text{H}_2} - k_{\text{H},\text{X}},$$

$$B = (k_{\text{H},\text{H}_2\text{O}} + K_6 k_{\text{OH},\text{H}_2})[\text{H}_2\text{O}] + k_{\text{H},\text{X}}(1 - [\text{H}_2\text{O}]) - k_{\text{OH},\text{X}}K_6[\text{H}_2\text{O}],$$

and

$$C = K_6[\text{H}_2\text{O}]^2 k_{\text{OH},\text{H}_2\text{O}} + K_6[\text{H}_2\text{O}]k_{\text{OH},\text{X}}(1 - [\text{H}_2\text{O}]).$$

It will be noted that the rate constants $k_{\text{H},\text{H}_2\text{O}}$ and k_{OH,H_2} appear in composite form because of the operation of the balanced Reaction (6) and only upper limits for these individual rate constants can be obtained. Measurements of k_0 as a function of $[\text{H}_2]$ will therefore provide values of A , B , and C . However, since $[\text{H}_2\text{O}]$ is practically constant in an isothermal group of hydrogen/oxygen/X flames, no values for individual rate constants can be obtained from A , B , and C alone. To obtain such individual values isothermal variations of $[\text{H}_2\text{O}]$ are required. This can be achieved by using steam as a diluent. For hydrogen/oxygen/steam flames Eq. (7) becomes

$$k_0([\text{H}_2] + K_6[\text{H}_2\text{O}])/2 = A'[\text{H}_2]^2 + B'[\text{H}_2] + C' \quad (8)$$

where

$$A' = (k_{\text{H},\text{H}_2} + K_6 k_{\text{OH},\text{H}_2\text{O}}) - (k_{\text{H},\text{H}_2\text{O}} + K_6 k_{\text{OH},\text{H}_2})$$

$$B' = (k_{\text{H},\text{H}_2\text{O}} + K_6 k_{\text{OH},\text{H}_2}) - (2K_6 k_{\text{OH},\text{H}_2\text{O}}),$$

$$C' = k_{\text{OH},\text{H}_2\text{O}}K_6.$$

Clearly, values of the three unknown rate constants can be obtained from steam flames and once these constants are known a complete analysis of hydrogen/oxygen/X flames can be made.

In a fuel-rich hydrogen/oxygen/carbon dioxide flame, carbon dioxide is partially reduced to carbon monoxide and, hence, four bulk species are generally present. Because of this the expression analogous to (7) and (8) is more complex and it has not proved possible to make a complete analysis of the recombination rates in flames diluted with carbon dioxide. The limited analysis which has been made is described in more detail later.

3. Experimental

3.1 Apparatus

The burner was a laminar-flow flat-flame burner of the type used previously and described else-

where.¹ It provided two concentric flames, the inner being the experimental flame and the outer serving as a shield against indrawn air. The burner was fitted with heating elements in the wall which enabled it to be heated to about 150°C for use with steam. It was mounted on a motor-driven carriage and could be raised or lowered at a uniform linear rate.

The atomic absorption equipment consisted of a narrow line source (hollow-cathode lamp) with an optical system of small f-number designed to give a narrow beam through the experimental part of the flame. The spatial resolution at the edges of the inner flame was <0.2 mm. The detector was an E.M.I. photomultiplier type 9592 used with an interference filter which isolated the lithium resonance line. The incident beam was modulated by mechanical chopping, and the photomultiplier output fed to a narrow-bandwidth phase-sensitive detection system. The output from this was presented on a pen-recorder. A continuous record of transmitted intensity of lithium resonance radiation as a function of distance from the reaction zone of each flame could therefore be obtained.

Traces of lithium were added to the inner flame as a fine mist of atomized solutions of lithium chloride. The atomizer was a pneumatic type driven by part of the diluent gas supply or, for the steam flames, by the hydrogen or oxygen supply. Because of the small flow rates available for atomization it was not possible to set up steam flames at temperatures below about 1800°K.

Gas supplies were of standard commercial purities and were metered through calibrated floatmeters to an accuracy of better than 2%.

Flames were set up in isothermal groups varying widely in composition. A set comprised ten to twelve flames varying from slightly fuel-rich to very rich (hydrogen/oxygen ~ 7). The sodium-line reversal method was used to measure flame temperatures which for an isothermal set were constant to ±40°K. Isothermal sets were set up at approximately 1600°, 1800°, and 2000°K. In addition a smaller group of flames were set up for calibration purposes in the region 2200°–2400°K with temperatures known to within 20°K.

Dry steam was generated at ≤200 psi in an electrically heated boiler and was maintained in a superheated state on its way to the burner, by passage through stainless steel pipes heated by the passage of a large current (~100 amp) through the pipe walls. Two pressure-reducing valves controlled the pressure immediately above two critical orifices. These orifices were calibrated by condensing the steam passed and weighing the water.

Sets of steam flames were set up at 1840° and 1990°K, and in addition a smaller group of hotter, calibration, flames in the region 2200°–2400°K.

3.2 Linearity of the Atomic Absorption Spectroscopy System

A number of preliminary experiments were carried out to check the linearity between $\ln(I_0/I_t)$ and C_{Li} and the constancy of $\ln(I_0/I_t)$ over the range of hollow cathode lamp currents used.

The absence of scattering was demonstrated by an experiment with a thallium lamp. No variation in transmitted light as a function of flame height was observed.

3.3 Calibration of the System

Although the quantity θ in expression (3) can be found by a combination of experiment (to determine the atomizer efficiency) and calculation¹² (to determine the spectroscopic parameters of the lithium resonance line in the flame), the accuracy of such a procedure is not great. A more satisfactory approach is the direct determination of θ experimentally by use of Eq. (3) in a flame where $[H]$ is known.

It has been established¹ that in reasonably hot flames ($T > 2200^\circ K$) equilibrium is attained moderately close to the reaction zone i.e. within 2–3 cm. Measurements of $\ln(I_0/I_t)$ in such flames, combined with calculated values of $[H]$, then enable θ to be determined. A small correction was made to allow for the temperature-dependence of θ . This has been discussed elsewhere.¹²

4. Results

Reciprocal hydrogen-atom concentrations in each flame were calculated from the measured $\ln(I_0/I_t)$ values as functions of time downstream from the reaction zone. A typical record of I_t as a function of distance is shown in Fig. 1. The results for one set of flames are presented in Fig. 2. Several features of the plots in Fig. 2 will be noted, and the same characteristics applied to all the isothermal sets.

(a) At high hydrogen-atom concentrations the plots show distinct curvature. This is interpreted as being due to diffusion of hydrogen atoms and to the effect of the small increase in temperature over this range on K_{Li} . In flames at temperatures of $1600^\circ K$ and below the curvature is very pronounced and clearly diffusion is a major factor at these temperatures. Because of the difficulty of allowing for diffusion in multicomponent mixtures no further work on flames at $1600^\circ K$ or below was undertaken.

(b) The differences in observed rates between

the various flames in Fig. 2 are fairly small. This again is a feature of all the sets of flames studied. At this stage it is qualitatively clear that there are no marked differences between hydrogen and the diluent gas molecules in their efficiencies as third bodies.

5. Analysis of Experimental Results

(Note added in proof. Work done subsequent to the presentation of this paper has shown that some of the measured recombination rates are too low because of neglect of the reverse, dissociation reaction. Preliminary recalculations indicate that the result for k_{OH,H_2O} reported in this paper is too low. Full details, together with revised values for all the rate constants, will be published at a later date.)

It will be observed that both Eqs. (7) and (8) are of the same form—i.e., $k_0([H_2] + K_6[H_2O])$ is a quadratic function of $[H_2]$. Since the parameters involved are less complex for the steam flames than for diluent flames the former are treated first. No significant differences were found between the results at the two temperatures and in Fig. 3 mean values of $k_0([H_2] + K_6[H_2O])$ are plotted against $[H_2]$ for all the steam flames. The curvature term A' is poorly defined and because of this we have used the value for k_{H,H_2} of $0.20 \times 10^{-32} \text{ ml}^2 \text{ molecule}^{-2} \text{ sec}^{-1}$ at $1915^\circ K$ found by Hurle, Jones, and Rosenfeld^{8,14} to give an im-

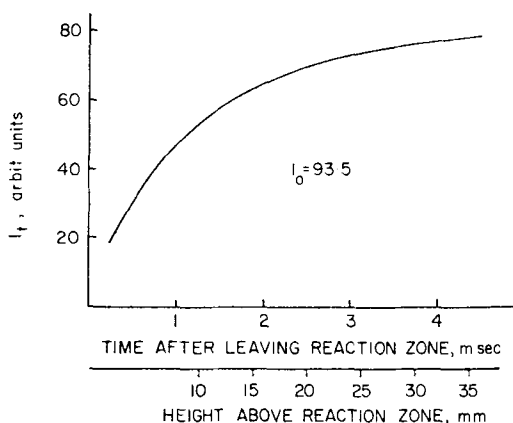


FIG. 1. Traced recording of intensity of Li 6707 Å light transmitted through a premixed laminar flame of unburned hydrogen/oxygen/nitrogen proportions 3.12/1/4.76 respectively.

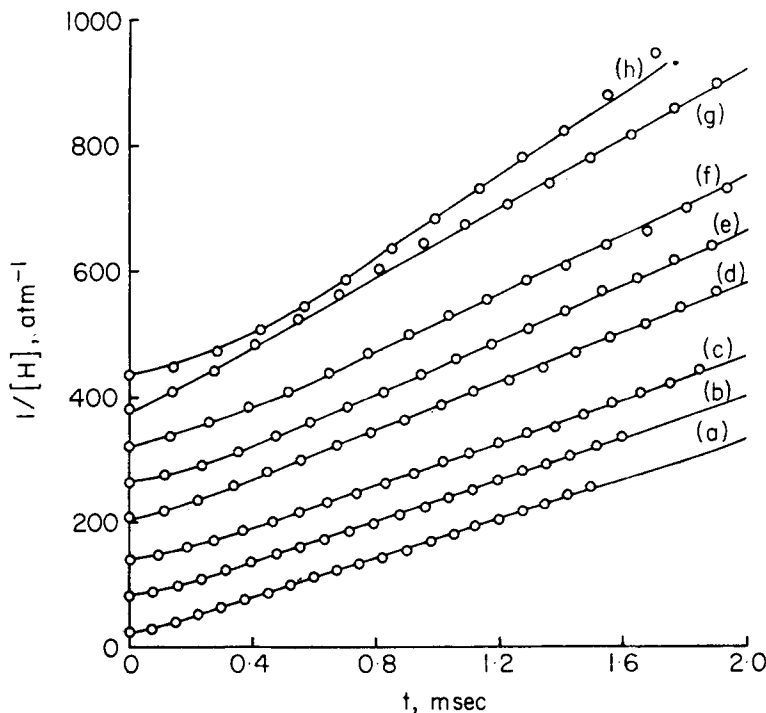


FIG. 2. Plots of $1/[H]$ against t for an isothermal set of hydrogen/oxygen/nitrogen flames at 1980°K . Each plot is displaced upwards by a successive amount of 50 atm^{-1} . The unburned hydrogen/oxygen/nitrogen proportions are: (a) 5.08/1/2.76; (b) 4.93/1/2.91; (c) 4.57/1/3.35; (d) 3.85/1/3.98; (e) 3.36/1/4.48; (f) 3.12/1/4.76; (g) 2.57/1/5.27; (h) 2.13/1/5.61.

proved fitting to the data. This datum defines a point on Fig. 3 such that $k_0/2 = k_{\text{H},\text{H}_2} = A' + B' + C'$ at $[\text{H}_2] = 1$ and hence gives a more precise value for A' . The curve through the points

on Fig. 3 has been obtained by a least-squares analysis with equal weight given to each point and subject to the constraint that $A' + B' + C' = k_{\text{H},\text{H}_2}$. The results derived from Fig. 3 which

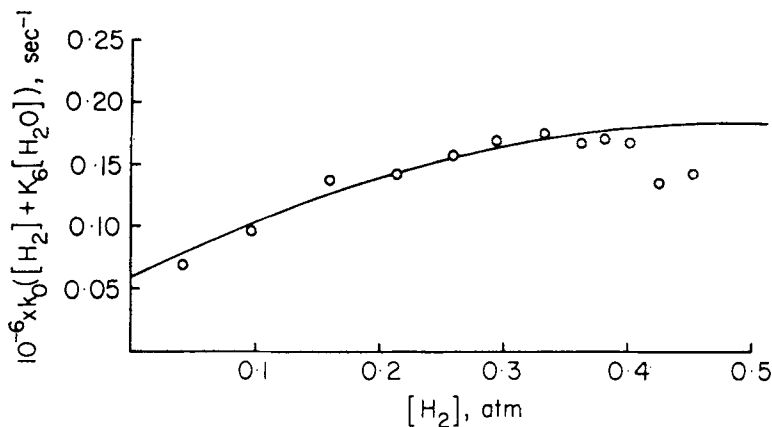


FIG. 3. Plot of $k_0([\text{H}_2] + K_6[\text{H}_2\text{O}])$ against $[\text{H}_2]$ for a series of hydrogen/oxygen/steam flames at a mean temperature of 1915°K .

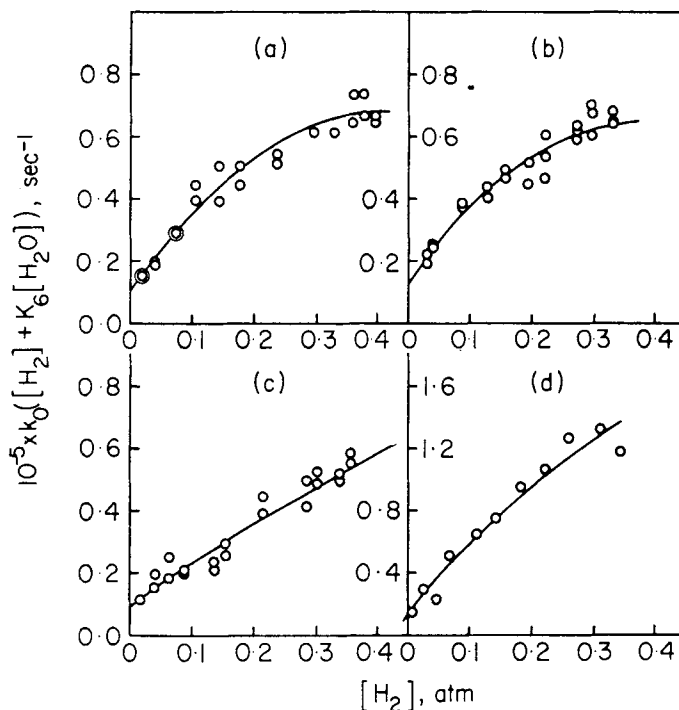


FIG. 4. Plots of $k_0([H_2] + K_6[H_2O])$ against $[H_2]$ for isothermal sets of flames: (a) hydrogen/oxygen/nitrogen flames at 1980°K; (b) hydrogen/oxygen/helium flames at 1950°K; (c) hydrogen/oxygen/argon flames at 1790°K; (d) hydrogen/oxygen/carbon dioxide flames at 1780°K.

refer to the mean temperature of 1915°K, are

$$k_{OH,H_2O} = 2.4 \times 10^{-32} \text{ ml}^2 \text{ molecule}^{-2} \text{ sec}^{-1}$$

$$(k_{H,H_2O} + K_6 k_{OH,H_2})$$

$$= 2.1 \times 10^{-32} \text{ ml}^2 \text{ molecule}^{-2} \text{ sec}^{-1}$$

with estimated error factors of 1.5 and 2 respectively.

Values of k_0 for the sets of hydrogen/oxygen flames diluted with nitrogen, argon or helium were plotted in the same way. A selection of typical plots is shown in Fig. 4. From these plots, values of A , B , and C for each set of flames were obtained and these, together with the results given above, enabled values for the other rate constants to be derived.

The evaluation of single rate constants from these values of A , B , and C can be carried out in several ways. However, because (a) some of the expressions for these parameters involve differences and (b) successive operations involve previously determined rate constants, we have chosen the method involving the least number of steps in order to avoid excessive cumulative

errors. The procedure adopted was as follows:

(i) Evaluate $k_{H,X}$ from A making use of the value of the adopted value of k_{H,H_2} .

(ii) Evaluate $k_{OH,X}$ from C and the value of k_{OH,H_2O} determined from the steam flames. Although the value of k_{OH,H_2O} refers to a temperature of 1915°K, the relatively small temperature-dependence of this rate constant,¹⁵ leads to no significant error being introduced by this procedure.

This method avoids making use of the term B in Eq. (11), since here two previously determined quantities must be used to find a rate constant, either $(k_{H,H_2O} + K_6 k_{OH,H_2})$ and $k_{H,X}$ to give $k_{OH,X}$ or $(k_{H,H_2O} + K_6 k_{OH,H_2})$ and $k_{OH,X}$ to yield $k_{H,X}$. Consideration of the probable errors in B and in these constants shows that this procedure is not a satisfactory one.

Table I gives values of $k_{H,X}$ and $k_{OH,X}$ at ~1800° and ~2000°K evaluated by procedures (i) and (ii). In view of the fact that changes in these termolecular rate constants with temperature are relatively small, the differences between the values at 1800° and 2000°K are almost cer-

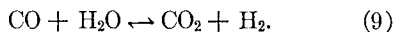
TABLE I

Values of termolecular rate constants for nitrogen, helium, argon, and carbon dioxide/carbon monoxide as third bodies

Diluent X	$k_{H,X} \times 10^{32}$, ml ² molecule ⁻² sec ⁻¹			$k_{OH,X} \times 10^{32}$, ml ² molecule ⁻² sec ⁻¹		
	1800°K	2000°K	Mean 1900°K	1800°K	2000°K	Mean 1900°K
Nitrogen	0.57	1.48	1.02	1.44	1.17	1.30
Helium	0.95	1.66	1.30	1.75	2.18	1.96
Argon	0.38	0.83	0.60	2.41	1.26	1.83
Carbon dioxide (see text)	1.54	1.28	1.41	—	—	< ~0.5

tainly not significant.¹⁵ Mean values of $k_{H,X}$ and $k_{OH,X}$ at 1900°K are therefore also given in Table I. The error in these values is estimated to be not greater than a factor of two.

As stated earlier the analysis of rate data obtained from flames containing carbon dioxide as diluent presents added complications. Four rate constants involving carbon monoxide and carbon dioxide take the place of the two involving the diluents discussed previously, although two of the four form a second inseparable sum $K_9 k_{H,CO_2} + K_9 k_{OH,CO}$ where K_9 is the equilibrium constant for the balanced reaction



The expression analogous to Eqs. (7) and (8) becomes a cubic in $[H_2]$. Examination of the accuracy and reproducibility of the rate data showed that these do not justify fitting to an expression of such detailed form.

The procedure adopted therefore was to treat the data from these flames in the same way as those with an inert diluent, the total diluent concentration being regarded as $[CO] + [CO_2]$. The requirement for the application of Eq. (7), that the water concentration is constant, is approximately satisfied, e.g. for the 1970°K set of carbon dioxide-diluted flames, $[H_2O] = (0.44 \pm 0.03)$ atm.

The rate data from the plots of $1/[H]$ against t for these flames, when fitted to Eq. (7) as in the case of data from flames with inert diluents, lead to the plot shown in Fig. 4(d) for the isothermal set of flames at 1780°K. Certain qualitative conclusions regarding the size of the true rate constants can be deduced from the plots.

(a) Neither carbon monoxide nor carbon dioxide is more efficient than the other third bodies present in the $H + OH$ recombination.

(b) Carbon dioxide cannot be substantially more efficient than the other bulk species for hydrogen-atom recombination since the values of the overall rate constants would show a decrease with increasing values of $[H_2]$ if this were the case.

An analysis of these flames, and also a set at 1970°K, led to the values for $k_{H,X}$ shown in Table I. It should be noted that these rates are effective ones, because of the procedure described above, and are not the actual rates of recombination with carbon monoxide and carbon dioxide as third bodies, unless these are equal. It proved impossible to obtain any values for $k_{OH,X}$ from these flames because the rate of recombination in the near stoichiometric flame can be completely accounted for within experimental accuracy by $H + OH + H_2O \rightarrow 2 H_2O$ and there are no significant contributions from carbon dioxide and carbon monoxide. An upper limit for the rates of these reactions, which would have led to measurable differences in the values of the intercepts, is given in Table I.

6. Comparison with Other Results

Previous values for recombination rate constants have been obtained by shock-tube techniques, by discharge-flow methods and by flame studies. The first two methods have provided values mainly for $k_{H,X}$, where X is an inert gas atom or hydrogen, and of the previous flame studies only those by Dixon-Lewis *et al.*² and by Rosenfeld and Sugden³ have separated the observed recombination rates into contributions from individual reactions, as is done in this present work. In general, the agreement between our results and those of Refs. 2 and 3 is not very

good even after allowance is made for differences in definitions of rate constants (k_H and k_{OH} values in Ref. 2 and k_H and $k_{H,H_2O} + K_6 k_{OH,H_2}$ values in Ref. 3 should be divided by two for comparison with the values obtained in this work). The principal difference is in the relative importance of Reactions (1) and (2); the k_{OH,N_2} and k_{OH,H_2O} values given in Refs. 2 and 3 are about an order of magnitude larger than those reported here, while the k_{H,N_2} values are smaller. In support of the present values it should be noted that a larger range of compositions has been studied in this work. Furthermore, the analysis has been carried out statistically and without any assumptions apart from the use of a well established value for k_{H,H_2} . The value of $4 \times 10^{-32} \text{ ml}^2 \text{ molecule}^{-2} \text{ sec}^{-1}$ obtained by Zeegers and Alkemade⁷ for k_{OH,N_2} is in better agreement with our value.

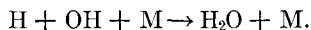
Agreement between the present values and with comparable shock-tube results is generally more satisfactory. For $k_{H,Ar}$ several studies¹⁵ indicate a value of ca. 0.1×10^{-32} at about 3500°K and of 0.16×10^{-32} at 1700°K.¹⁶ A more recent study¹⁴ has given a value of 0.5×10^{-32} at 1900°K which is in good agreement with the present one of 0.6×10^{-32} at 1900°K. For $k_{OH,Ar}$ values of 1.5×10^{-32} and 1.6×10^{-32} previously reported^{9,16} are in good agreement with our value of $1.8 \times 10^{-32} \text{ ml}^2 \text{ molecule}^{-2} \text{ sec}^{-1}$.

ACKNOWLEDGMENTS

We are grateful to Professor T. M. Sugden, F.R.S., for helpful discussions and to Mr. A. Prothero and Mrs. A. C. Rowlands for computer programming and least-squares analyses.

COMMENTS

J. Troe, Institut für Physikalische Chemie der Universität Göttingen. There was some evidence from earlier shock-tube work, for instance by Getzinger,¹ that water is much more effective than Ar as a third body for



This is in contrast to your results. How sure are you of your results and how do you estimate the accuracy of your values? Does your accuracy rule out pronounced differences between H_2O and Ar third-body efficiency? Further, is the remaining factor-of-3 discrepancy between your values and our results, derived from H_2O -dissociation experiments,² within the limits of accuracy?

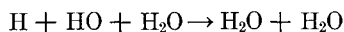
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Authors' reply. We can find no reference to a value for the rates of



determined by shock-tube work in the paper by Getzinger and Blair.¹ The values given there refer to earlier flame studies. As pointed out in our paper we are not in agreement with their

studies and find values which are about ten times smaller, as did Olschewski *et al.*² On the other hand, we are in substantial agreement with Getzinger's values for $k(\text{OH}, \text{N}_2)$ and $k(\text{OH}, \text{Ar})$.

We are unable to comment on the difference between our result for $k(\text{OH}, \text{Ar})$ and that obtained in Ref. 2, since no clear indication of the error was given in that work. Since our value for this rate constant is derived from the relatively well-defined intercepts of our plots (Fig. 4), and in view of the close agreement with Getzinger's value³ ($1.5 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$) and that of Browne *et al.*⁴ ($1.3 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$) we think that the difference between our value and that of Ref. 2 lies outside our limits of experimental error.

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G. Dixon-Lewis, University of Leeds, Leeds, England. I have made some fairly realistic com-

puter calculations on a hydrogen-nitrogen-oxygen flame having an initial temperature of 300°K and a final temperature of 1950°K, quite close to that of the flames studied in this paper. Although the calculations are not yet absolutely complete in details of the reaction mechanism, the indications are that the maximum radical concentration occurs at between 1200° and 1300°K. Some 3–4 mm later, the temperature has risen to within about 150° of its final value, and beyond this the temperature rise is slower. Since temperature is an important parameter in their expression for the H-atom concentration, could the authors tell us what temperature changes were involved in their region of measurement?

Authors' reply. In our work, in order to minimize temperature and diffusion effects, the observed second-order rate constants for the decay of hydrogen atoms were calculated excluding those concentrations measured nearer the reaction zone than 6 mm. Previous experimental work¹ indicates that, at this distance from the reaction zone, the temperature is 60°–80°K below its final value, a difference which is in reasonable agreement with the calculations of Dixon-Lewis. Since temperature affects both the $1/[\text{H}]$ and the time scales in the same direction, the effect on the slopes of the plots of $1/[\text{H}]$ against time is considered to be small.

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