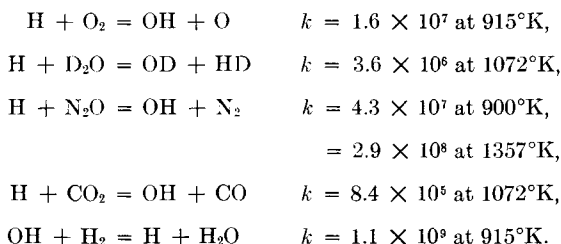# SOME REACTIONS OF HYDROGEN ATOMS AND SIMPLE RADICALS AT HIGH TEMPERATURES

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Investigations of the structure of flames supported by a hydrogen–nitrogen–oxygen and a hydrogen–nitrogen–nitrous oxide mixture on an Egerton–Powling-type flat-flame burner have been used to derive information on the elementary reactions involved. At atmospheric pressure, the flames have final temperatures of 1072° and 1573°K, respectively. Temperature and composition profiles are obtained by probing, and both concentration diffusion and thermal diffusion are considered in the subsequent analysis. Hydrogen atoms are estimated by added D_2, D_2O, or chemiluminescence. Further results were obtained by adding traces of nitrous oxide and carbon dioxide, respectively, to the oxygen supported flame.

Rate constants were found as follows (1 mole^{-1} sec^{-1})

$$H + O_2 = OH + O \qquad k = 1.6 \times 10^7 \text{ at } 915°K,$$

$$H + D_2O = OD + HD \qquad k = 3.6 \times 10^6 \text{ at } 1072°K,$$

$$H + N_2O = OH + N_2 \qquad k = 4.3 \times 10^7 \text{ at } 900°K,$$

$$= 2.9 \times 10^8 \text{ at } 1357°K,$$

$$H + CO_2 = OH + CO \qquad k = 8.4 \times 10^5 \text{ at } 1072°K,$$

$$OH + H_2 = H + H_2O \qquad k = 1.1 \times 10^9 \text{ at } 915°K.$$

Apparent second-order rate constants for the recombination reactions of H + H and H + OH in the burned gas of the particular flames are also given, and third-order rate constants derived over a limited composition range.

Prediction of reaction rates in combustion systems necessitates an accurate knowledge of rate constants at high temperatures. This is particularly important in the case of hydrogen atoms, which play an important role in many of the chain propagating steps. The methods used to obtain information on reactions of hydrogen atoms at intermediate and high temperatures include, in order of increasing temperature, (a) studies of reaction rates and explosion limits in systems such as hydrogen–oxygen (b) flame studies, and (c) shock tube investigations. In certain cases, for example the chain-branching reaction of hydrogen atoms with oxygen, it has now become possible to combine results from all three of these methods with results at about room temperature to cover an extended temperature range. Clearly the more extended this range the more accurate are the reaction-rate parameters.

This paper describes an examination of some of the reactions occurring in a hydrogen–nitrogen–oxygen flame and a hydrogen–nitrogen–nitrous oxide flame. At atmospheric pressure, slow-burning hydrogen-rich flames supported by suitable mixtures of these gases may be stabilized on an Egerton–Powling-type flat-flame burner.[1,2] They have final flame temperatures around 1100°K for oxygen and 1500°K for nitrous oxide, and their burning velocities and temperature and composition profiles may be measured sufficiently accurately for the determination of reaction rates with reasonable precision.

In this work, in addition to a study of the main flame processes, the decay of traces of nitrous oxide and carbon dioxide added to the hydrogen–nitrogen–oxygen flame has been studied, together with the rates of formation of HD when traces of heavy water are added to the flames.

Relation Between Flame Parameters and Reaction Kinetics

Flat flames stabilized on an Egerton–Powling-type burner represent approximately uni-dimensional flowing reaction systems. If M is the mass

burning velocity and G_i is the weight fraction of species i in the mass rate of flow, then MG_i represents a mass flux of i. Continuity considerations require, first, that M is constant throughout the flame, and second, that the first distance derivative of the mass flux of species i be equal to its chemical rate of formation. The continuity equation for the species is, therefore,

$$M \, dG_i/dy = m_i(\partial n_i/\partial t)_{\text{chem}}, \qquad (1)$$

where y denotes distance in the direction of motion through the flame, m_i is the molecular weight of i, and $(\partial n_i/\partial t)_{\text{chem}}$ is its rate of formation in mole cm^{-3} sec^{-1}.

Now the measured quantities in the flame, in addition to burning velocity, are the temperature T and the weight fractions w_i of each species in the gas at a number of distances through the flame. The w_i are related with the molar species concentrations n_i by means of equations such as

$$[n_i] = \rho w_i/m_i \qquad (2)$$

where ρ is density, while the mass fluxes MG^i may now be seen to consist of two parts: (i) a convection term Mw_i representing the mean mass flow of i, and (ii) a diffusion flux j_i. The G_i are, therefore, expressed in terms of the w_i by means of the diffusion equations (3)

$$MG_i = Mw_i + j_i. \qquad (3)$$

In the flames considered here, where there is a large difference of molecular weight as between the hydrogen and the other constituents, thermal diffusion has been considered in evaluating the j_i. The complete expression for the j_i is, therefore, given by

$$j_i = \frac{\rho_{\text{molar}}}{\sum m_i X_i} \sum_{j \neq i} m_i m_j D_{ij} \frac{dX_j}{dy} - D_i^T \frac{d \ln T}{dy} \qquad (4)$$

where the D_{ij} and D_i^T denote the multicomponent diffusion coefficients and multicomponent thermal diffusion coefficients, respectively, while X_i represents mole fraction. Expressions for obtaining the D_{ij} and D_i^T from the binary diffusion coefficients $\mathfrak{D}_{ij}$ and other properties of the mixtures are given by Hirschfelder, Curtiss, and Bird.[3] When the species i was only a trace component, the form of

$$j_i = -\rho D_i \, dw_i/dy - D_i^T \, d \ln T/dy \qquad (5)$$

was used for j_i, where

$$1/D_i' = \sum_{j \neq i} X_j/\mathfrak{D}_{ij}.$$

Experimental Methods

The experimental methods employed are es-

sentially similar to those described previously,[4] and consist of methods for measuring the temperature and composition profiles. To avoid having to store gas samples abstracted from the flame a continuous-flow sampling system was used, and a small proportion of the sample was leaked directly into an A.E.I. MS 10 mass spectrometer. As before, quartz probes were used to sample directly from the flame. Gases were measured as ratios of peak heights to that of nitrogen, and calibration factors were applied to allow for discrimination effects in the mass spectrometer. The measured ratios were then evaluated on the basis that the sum of the mole fractions of the constituents must be unity.

In order to correlate the various profile measurements the plane of the schlieren maximum was used as the reference plane on the distance coordinate for all the flames studied.

Temperature profiles were measured using a quartz-coated platinum/13% rhodium–platinum thermocouple of suitable design as previously described.[4] The maximum radiation correction in the hydrogen–nitrogen–oxygen flame was 12°K, but in the hotter nitrous oxide-supported flame it was about 100°K.

Results

(a) Hydrogen–Nitrogen–Oxygen Flames

(i) *Profiles of Major Species.* A number of features of a low temperature hydrogen–nitrogen–oxygen flame, containing initially 4.604% oxygen, 18.83% hydrogen, and 76.57% nitrogen, have been described previously.[4] With the refined analytical technique since employed, however, some
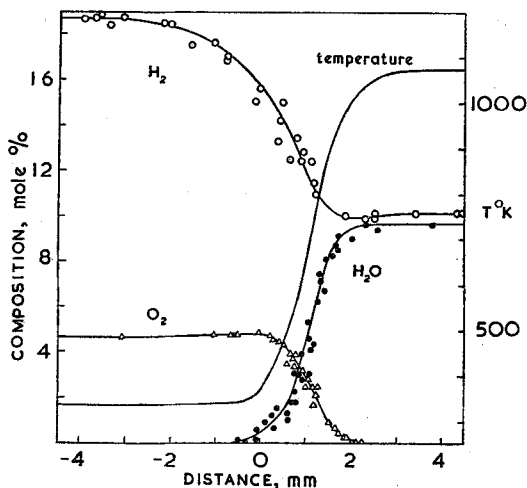

FIG. 1. Temperature and composition profiles for stable species in the hydrogen–oxygen flame.

small inaccuracies in the earlier composition profiles for the stable species, particularly hydrogen in the early part of the flame, have become apparent. These profiles were not used in the analysis previously described. Figure 1 shows the new composition profiles for hydrogen, oxygen, and steam, together with the temperature profile. Using diffusion data, where available, consistent with the high temperature results of Walker and Westenberg,[5] the magnitude of the various fluxes were evaluated. Figures 2 and 3 show those for hydrogen and oxygen, respectively, and the MG fluxes are seen to be in good agreement. Some interesting general results are worthy of mention: First, due to the high diffusion coefficient of hydrogen, and its consequent early diffusion towards the reaction zone, the oxygen mole fraction initially *increases* slightly before decreasing. Second, in this flame the thermal diffusion flux of hydrogen augments the concentration diffusion flux, and is up to 25% of the latter in value. Third, the thermal diffusion of oxygen is in the same direction as that for hydrogen. This appears to be partly connected with the low oxygen concentration since only nitrogen has a thermal diffusion flux towards the cold gas in this flame.

The gradient of the MG_{O_2} flux at a point in the flame gives an over-all rate of removal of oxygen at that point. The maximum value of this gradient corresponds to $-[\partial[O_2]/\partial t]_{chem} = 0.26$ mole l^{-1} sec^{-1} at about 915°K with

$$-(1/[O_2])[\partial[O_2]/\partial t]_{chem} = 3050 \text{ sec}^{-1}.$$

Due to some uncertainty about the shape of the oxygen profile when the oxygen concentration is very small, it is possible that the rates
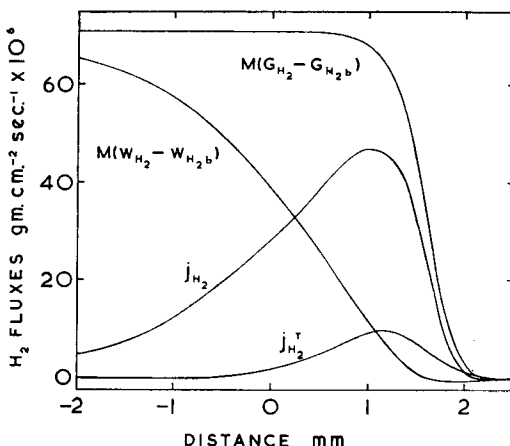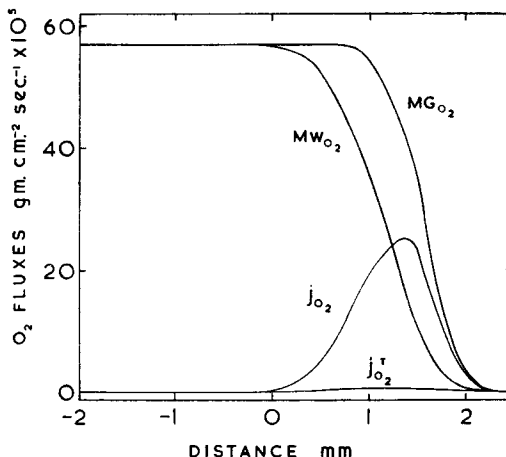

FIG. 3. Fluxes of oxygen in the hydrogen–oxygen flame.

quoted may need some revision upward. It is very unlikely, however, that this would be by more than about 10%.

In the same way, $-(1/[H_2])[\partial[H_2]/\partial t]_{chem} = 385$ sec^{-1} at 915°K.

(ii) Hydrogen-Atom Concentration. The maximum hydrogen atom concentration in the above flame has already been estimated[4] by adding a trace of deuterium to the flame gases and measuring the build-up of HD due to the exchange Reactions (I) and (II).

$$H + D_2 \rightleftharpoons HD + D \qquad (I)$$

$$D + H_2 \rightleftharpoons HD + H. \qquad (II)$$

The precision of the method suffers from some difficulties due to the low concentration of D_2 at the position of maximum rate of HD formation, and a reassessment of the results,[6] which has included a small allowance for the rates of the back reactions, has led to an upward revision of the maximum H-atom concentration to 3.5×10^{-5} mole l^{-1} at around 900°K.

(iii) Flame with Traces of Sodium Salts or Heavy Water Added. When heavy water is added to the flame gases there is again a build-up of HD due to a series of reactions triggered by Reaction (III).

$$H + D_2O = OD + HD. \qquad (III)$$

If the rate of build up of HD is measured, together with the corresponding concentrations of H and D_2O, then k_3 can be found. Experimentally, D_2O is difficult to measure. It can, however, be eliminated from the rate expression by means of a generalization[4] of the kinetic analysis proposed

FIG. 2. Fluxes of hydrogen in the hydrogen–oxygen flame.

by Fenimore and Jones.[7] The assumptions involved are considered to be reasonably valid, except in the very early stages of the reaction.

Due to the considerably higher activation energy of Reaction (III) compared with Reaction (I), the regions of HD formation by the two reactions do not overlap in the flame, its formation from D_2O occurring further into the burned gas region. Here there is no direct measure of [H]. The D_2O experiments, therefore, only give values of k_3 [H] as a function of distance in the burned gas. Between the two relevant regions, recombination of atoms and radicals takes place by Reactions (IV) and (V), together with rapid equilibration of H and OH by the bimolecular process (VI).

$$H + \; H + M = H_2O + M \qquad (IV)$$

$$H + OH + M = H_2O + M \qquad (V)$$

$$OH + H_2 \rightleftharpoons H_2O + H. \qquad (VI)$$
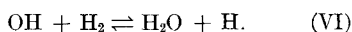
However, Padley and Sugden[8] have shown that relative H-atom concentrations in the burned gas region of low temperature flames of this type may be measured by the intensity of chemiluminescence when small amounts of sodium salts are added. The chemiluminescence is due to excited sodium atoms formed by Reactions (VII) and (VIII)

$$H + \; H + Na = H_2 \; + Na^* \qquad (VII)$$

$$H + OH + Na = H_2O + Na^*. \qquad (VIII)$$
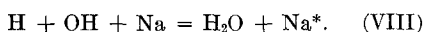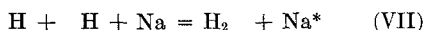
Hence if Reaction (VI) maintains the ratio [H]/[OH] at its equilibrium value then

$$I_{Na} \propto [H]^2 \quad \text{or} \quad I_{Na} \propto (k_3 [H])^2.$$

By suitably scaling the values of $(k_3 [H])^2$, they can be fitted accurately on to the intensity curve. If it is then assumed that the maximum in the latter corresponds with the maximum H-atom concentration in the flame, then the calibration is complete. Such a fit leads to the value

$$k_3 = 3.6 \times 10^6 \text{ l mole}^{-1} \text{ sec}^{-1} \text{ at } 1072^\circ K.$$

(iv) *Recombination Reactions in the Burned Gas.* In a flowing reaction system containing a small concentration of H atoms, [H] is related to distance by means of

$$\int [\partial[H]/\partial t]_{chem} \, dy = S[H] - D_H \, d[H]/dy,$$

$$(9)$$

where S is the linear flow velocity. For a fixed burned gas composition, if [H]/[OH] is maintained at its equilibrium value, then the chemical rate of formation of H atoms is given by

$$[\partial(H)/\partial t]_{chem} = -k_a[H]^2, \qquad (10)$$

where k_a is an apparent second-order recombination constant for the particular composition. Hence k_a may be determined from the calibrated chemiluminescence profile or from the values of $k_3[H]$ from D_2O experiments. Using the new maximum H-atom concentration of 3.5×10^{-5} mole l^{-1}, the apparent second order constant k_a for the flame under consideration becomes 3.4×10^7 l mole^{-1} sec^{-1} at $1072^\circ K$ (burned gas composition approximately $8N_2 + 1H_2 + 1H_2O$). The temperature variation is probably small (with a "negative activation energy"), so that this is in excellent agreement with the value 3.0×10^7 l mole^{-1} sec^{-1} recently quoted by Rosenfeld and Sugden[9] for the composition $8N_2 + 2H_2O + 1.5H_2$ at $1309^\circ K$.

If the composition entering the flame is adjusted to give a number of burned gas compositions having a common flame temperature, the constants k_a may, with some assumptions, be resolved into their constituent third-order rate constants. The measurements previously described by Dixon-Lewis, Sutton, and Williams[10] have now been extended by further work using D_2O, and an analysis of the complete system by the methods previously described[6] gives, at $1072^\circ K$,

$$k_4^{N_2} = k_4^{H_2O} = 1.7 \times 10^9,$$

$$k_4^{H_2} = 1.1 \times 10^{10},$$

and

$$k_5^{N_2} = k_5^{H_2O} = 1.1 \times 10^{11} \text{ l}^2 \text{ mole}^{-2} \text{ sec}^{-1}.$$

Here the agreement with our own previous figures is not so good. The reason for this is to be found in the small range of burned gas compositions which could be studied, so that the third-order constants are very sensitive to small changes in the k_a's. This difficulty is reflected particularly in the much higher third body efficiencies of H_2 relative to N_2 as compared with those previously obtained, and coupled with this, is the fact that $k_4^{N_2}$ is now reduced to half of its previous value, giving a much higher apparent ratio $k_5^{N_2}/k_4^{N_2}$.

(v) *Addition of a Trace of Nitrous Oxide to the Flame.* Nitrous oxide added to the rich hydrogen–oxygen flame will disappear principally by Reaction (IX).

$$H + N_2O = OH + N_2 \qquad (IX)$$
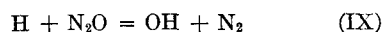
A small quantity (0.306%) of nitrous oxide was, therefore, added to the main flame and the oxygen concentration reduced slightly to compensate

for the combustion of the nitrous oxide. The rate of disappearance of nitrous oxide in the reaction zone obtained by application of the flux equations is found to give $-(1/[N_2O])[\partial[N_2O]/\partial t]_{chem} = 1490\ sec^{-1}$, again at about $900°K$ where $H = 3.5 \times 10^{-5}$ mole l^{-1}. Hence:

$$k_9 = 4.3 \times 10^7\ l\ mole^{-1}\ sec^{-1}\ at\ 900°K.$$

(vi) *Addition of a Trace of Carbon Dioxide.* Addition of carbon dioxide permits a study of the forward Reaction (X),

$$H + CO_2 = OH + CO \qquad (X)$$

which essentially parallels reaction (III) though having a somewhat slower rate. A small quantity of nitrogen (0.615%) in the unburned gases was replaced by carbon dioxide, and the rate of disappearance of carbon dioxide was followed in the burned gas region of the flame. In the region of maximum over-all rate of carbon dioxide disappearance it was found that the reverse reaction $(-X)$ was one-tenth as fast as the forward reaction. The derived $-[\partial[CO_2]/\partial t]_{chem}$ were corrected for this, and after dividing the corrected rate by $[CO_2]$ to give $k_{10}[H]$ for comparison with $k_3[H]$ from the D_2O experiments it was found

$$k_3/k_{10} = 4.3 \pm 0.5,$$

$$k_{10} = 8.4 \times 10^5\ l\ mole^{-1}\ sec^{-1}\ at\ 1072°K.$$

(b) *Hydrogen-Nitrogen-Nitrous Oxide Flame*

(i) In order to study the reaction between H atoms and nitrous oxide at a high temperature, a hydrogen–nitrogen–nitrous oxide flame without oxygen present was used. The flame studied had the unburned composition of 12.10% nitrous oxide, 21.46% hydrogen, and 66.44% nitrogen. With a burner matrix temperature of $399°K$, the theoretical flame temperature is $1577°K$, while the measured final-flame temperature, corrected for radiation losses, was $1573°K$. The burning velocity[2] is 6.8 cm sec^{-1} (gas velocity at $18°C/760$ mm).

The temperature profile and the composition profiles of the major species are shown in Figure 4. The same general features were observed as in the oxygen supported flame. Quantitatively, however, some difficulty was experienced in computing the diffusional flux of the nitrous oxide, and a very low temperature dependence had to be used for all diffusion coefficients involving nitrous oxide in order to avoid obtaining a negative $-[\partial[N_2O]/\partial t]_{chem}$ early in the flame. It is, of course, possible that such a negative "rate of disappearance" of N_2O is real, but we have preferred at this stage to assume not. On this basis the maximum gradient of the MG_{N_2O} flux
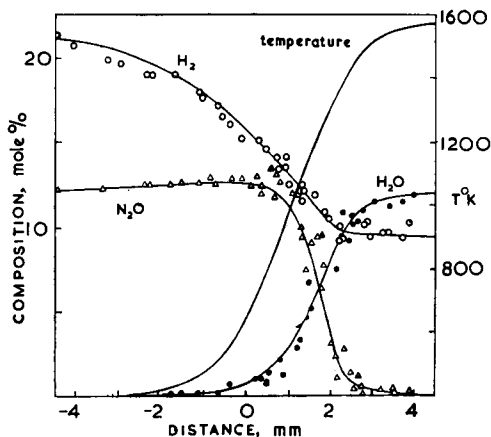

Fig. 4. Temperature and composition profiles for stable species in the hydrogen–nitrous oxide flame.

corresponds to $-[\partial[N_2O]/\partial t]_{chem} = 0.5$ mole l^{-1} sec^{-1} at $1357°K$ with

$$-(1/[N_2O])[\partial[N_2O]/\partial t]_{chem} = 2940\ sec^{-1}.$$

(ii) *Heavy Water Addition.* Because of the higher temperatures associated with this flame, the reaction of H with D_2O can be used to measure the H-atom concentration in the main reaction zone. At $1357°K$ in this flame we found $k_3[H] = 280\ sec^{-1}$.

On extending the analysis of the HD profile from D_2O into the burned gas region the ratio of k_a (the apparent second-order recombination constant for excess atoms and radicals) to k_3 was estimated to be 40.8.

Discussion

(a) *Hydrogen-Nitrogen-Oxygen Flame*

(i) *Reaction Between Hydrogen Atoms and Oxygen.* Before proper use can be made of over-all reaction rates measured in flames it is necessary to have a clear understanding of the flame mechanism. The simplest reasonable mechanism which may be assumed for the very rich hydrogen-oxygen flame comprises Reactions (VI), (XII), (XIII), and (IV) [computer studies having shown that Reaction (V) is unimportant in the very rich flame considered here].

$$OH + H_2 = H_2O + H \qquad (VI)$$

$$H + O_2 = OH + O \qquad (XII)$$

$$O + H_2 = OH + H \qquad (XIII)$$

$$H + H + M = H_2 + M \qquad (IV)$$
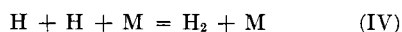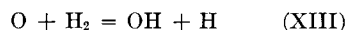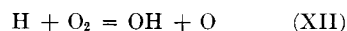
However, basic mechanisms for the hydrogen-oxygen reaction in KCl or B_2O_3 coated vessels
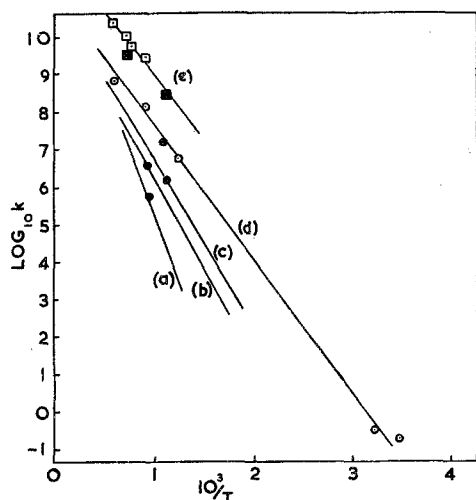
FIG. 5. Rate constants ($1 \text{ mole}^{-1} \text{ sec}^{-1}$) of the reactions of hydrogen atoms with (a) CO_2, (b) D_2O, (c) H_2O, (d) O_2, and (e) N_2O. ●,▨, this work. The values for (e) are multiplied by 10.

all involve the additional oxygen-consuming Reaction (XIV),

$$H + O_2 + M = HO_2 + M \qquad \text{(XIV)}$$

together with various means of disposing of the HO_2 formed. If we assume for the present that Reactions (XII) and (XIV) are the only reactions either removing or forming oxygen, then at 915°K we have

$$-(1/[O_2])[\partial[O_2]/\partial t]_{\text{chem}}$$
$$= k_{12}[H] + k_{14}[H][M].$$

A short extrapolation of second-limit results leads to $k_{12}/k_{14}[M] = 4.5$. The measured reaction rate and H-atom concentration then give

$$k_{12} = 1.6 \times 10^7 \text{ l mole}^{-1} \text{ sec}^{-1} \text{ at } 915°K.$$

This is in very satisfactory agreement with the values for Reaction (XII) displayed in Fig. 5. In combination with the agreement between Rosenfeld and Sugden[9] and ourselves regarding the apparent second-order radical recombination rate constant in the burned gas, it lends considerable support to the whole picture, and to the value of k_3 quoted earlier for the reaction between H and D_2O. There is, nevertheless, still a major problem—the subsequent reactions of HO_2. Discussion of these must be deferred for another occasion. However, computer studies[11] have shown that even in flames with high final temperatures, reaction paths via HO_2 are likely to be important, so that rate constants obtained from the "over-all" mathematical flame treat-

ments which neglect those paths should be treated with caution.

(ii) *Reaction* $OH + H_2 = H_2O + H$. An estimate of k_6 may be obtained from a preliminary measurement by Dixon-Lewis and Williams[4] of the OH concentration in the flame. This reached a maximum value of about 3×10^{-7} mole l^{-1}, to within a factor of 2. However, the interpretation of the light-absorption measurements depends on the f value assumed for the transition involved. This, in turn, depends, via the value for the equilibrium constant K_6, on the value assumed for the heat of formation of OH in the absorption calibration. In deriving the above, the calibration and method used by Kaskan[22] with $\Delta H_{298}° = 10.0$ kcal mole^{-1} was used. However, JANAF Thermochemical Tables quote $\Delta H_{298}° = 9.33$ kcal mole^{-1}. This would increase the OH concentration to 1.34 times the figure quoted earlier, that is, to 4.0×10^{-7} mole l^{-1}. A recent survey of the appropriate f values by Golden, Del Greco, and Kaufman[23] would tend to support the figures based on the JANAF table.

Whatever reasonable reaction mechanism is adopted in the flame, between 70% and 100% of the hydrogen consumed (we think nearer 100%) will react by Reaction (VI). The remainder will react with oxygen atoms, but this is compensated partly by atom recombination to give hydrogen. Assuming 100%, and using known values of H, H_2O, and the equilibrium constant to correct the reaction rate for the contribution of the reverse reaction, we find $k_6 = 1.1 \times 10^9$ l mole^{-1} sec^{-1} at 915°K, probably to within a factor of 2. Combining this with the value of 4.3×10^6 at 310°K quoted by Kaufman and Del Greco,[12] we obtain $E_6 = 5.2 \pm 0.6$ kcal mole^{-1}, with a mean log $A = 10.28$. This in turn gives a mean

$$k_{-6} = 9.1 \times 10^{10} \exp(-20,400/RT),$$

which is plotted in Fig. 5. At 1072°K, $k_{-6} = 6.7 \times 10^6$.

(iii) *Reaction* $H + D_2O = OD + HD$. From the hydrogen–oxygen flame we find

$$k_3 \text{ at } 1072°K = 3.6 \times 10^6 \text{ l mole}^{-1} \text{ sec}^{-1}.$$

In order to interpret the rate of formation of HD from D_2O at 1357°K in the hydrogen–nitrous oxide flame we need to estimate k_3 at the higher temperature. Due to zero-point energy differences between reactants and activated complex in Reactions (III) and (−VI) the activation energies will differ slightly. A number of alternative estimates could be made. If no effect of zero-point energy on Reactions (−III) and (VI)

is assumed, then the higher exothermicity (by 0.5 kcal mole^{-1}) of Reaction (III) would lead to $E_3 = 20.9$ kcal mole^{-1} and $k_3 = 6.2 \times 10^{10}$ exp $(-20,900/RT)$ l mole^{-1} sec^{-1}. This expression is plotted in Fig. 5.

(b) *Reactions in Hydrogen–Nitrogen–Nitrous Oxide Flame*

Our estimate of k_3 leads to values of 2.8×10^7 l mole^{-1} sec^{-1} at 1357°K and 8.1×10^7 at 1573°K. Using these in conjunction with the results from the hydrogen–nitrogen–nitrous oxide flame we find, assuming all the N_2O disappearance to be by reaction with H atoms

$$k_9 = 2.9 \times 10^8 \text{ l mole}^{-1} \text{ sec}^{-1} \text{ at } 1357°K.$$

This assumption is, of course, a slight approximation.[13] However, in this rich flame other reactions of nitrous oxide are very slight.

For recombination we find $k_a = 3.3 \times 10^9$ l mole^{-1} sec^{-1} at 1573°K. This value is much higher than the corresponding figure in the oxygen supported flame, and could be due to the participation of NO and NHO.[14]

(c) *Comparison with Other Kinetic Data*

Figure 5 shows a number of results by different authors for some of the reactions studied and the results obtained in this work.

$H + O_2 = OH + O$: This reaction has been discussed by Baldwin[15] who derived $k_{12} = 2.1 \times 10^{11}$ exp $(-16,600/RT)$ l mole^{-1} sec^{-1} as a mean of the following results (our own result has been added):

Schott and Kinsey[16]	1650°K	1.5×10^9
Fenimore and Jones[13]	1100°K	1.5×10^8
Baldwin and Cowe[17]	813°K	0.6×10^7
Kaufman and Del Greco[12]	310°K	0.334
Clyne and Thrush[18]	293°K	0.19
Present work	915°K	1.6×10^7.

The values given above are plotted in Fig. 5, and show excellent agreement among themselves.

$H + N_2O = OH + N_2$: This reaction has been studied previously by Fenimore and Jones[13] who found $k_9 = 4 \times 10^{11}$ exp $(-16,300/RT)$ on the basis of a value of k_3 which they have since revised. Their revised

$$k_9 = 3 \times 10^{11} \text{ exp } (-16,000/RT),[19]$$

and is the line shown in Fig. 5. Our own k_9 values are smaller than this, essentially a direct consequence of our smaller k_3.

$H + CO_2 = OH + CO$. Our ratio of rate constants $k_{10}/k_3 = (4.3 \pm 0.5)^{-1}$ is about three times

that which would result from the expression $k_{10}/k_3 = 3 \times$ exp $(-7800/RT)$ given by Fenimore and Jones.[20] This may be due to an apparent neglect of diffusion in their analysis. A later analysis by them[13] of the formation of CO_2 in a flame initially containing carbon monoxide includes a diffusion correction, and gives a result in slightly better agreement with our own. Our value of k_{10}, shown in Fig. 5, is somewhat above that of Fenimore and Jones, despite our smaller k_3. Using $k_{-10}/k_{10} = 270$ at 1072°K (consistent with the JANAF heat of formation for OH), our k_{-10} is quite close to that which would be obtained from Kondratiev's interpretation of the results of Avromenko and Lorentso[21] between 380° and 490°K. Kondratiev gives $k_{10} = 2.9 \times 10^9$ exp $(-5700/RT)$ l mole^{-1} sec^{-1}. It seems likely, however, that this agreement is fortuitous. Recent work by Ung and Back[25] gives $k_{-10}/k_6 = 0.032\pm0.004$ exp $(+4000 \pm 300/RT)$ between 473° and 623°K, while Baldwin[26] finds 0.33 for the same ratio at 773°K, and our results give 0.14 at 1072°K. The last two ratios are both lower than the Ung and Back expression would predict, but, between themselves, they again give $E_6 - E_{-10}$ of the order of 4 to 5 kcal mole^{-1}. All these results indicate an activation energy E_{-10} of the order of only 1 kcal mole^{-1}. We suggest $E_{-10} = 0.5 \pm 0.5$ kcal mole^{-1} with log $A_{-10} = 8.5 \pm 0.3$.

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COMMENTS

Prof. C. T. J. Alkemade (State University of Utrecht): The technique of determining relative H concentrations by chemiluminescence of Na requires that the concentration of ground state Na atoms is constant or that its variation with height is accounted for. In low-temperature flames, the formation of NaOH and/or NaO_2 (Kaskan, this Symposium p. 41) may induce a strong variation of atomic Na content with height. Such variation might be unambiguously determined by absorption measurements at the Na–D doublet. Has the effect of varying Na concentration been taken into account in the work reported?

Dr. G. Dixon-Lewis: In rich flames, such as are discussed in this paper, the oxygen concentration in the burned gas is virtually zero, and even at the maximum reaction rate in the flame it is very small. The formation of NaO_2 as suggested by Kaskan is, therefore, not likely in large amounts at any stage. The formation of NaOH by Equilibrium (I) is a possibility.

$$Na + H_2O \rightleftarrows NaOH + H. \qquad (I)$$
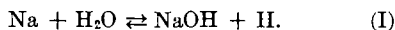
However, Smith and Sugden [Proc. Roy. Soc. (London) *A211*, 58 (1952)] find that NaOH is unstable and that sodium gives negligible compound formation in the burned gas from rich flames. Kaskan also finds difficulties in accounting for alkali-metal-atom concentrations in lean flames when hydroxide formation by Equilibrium (I) is assumed.

In the work on chemiluminescence briefly mentioned in this paper, it was found [Discussions Faraday Soc. *33*, 205 (1962)] that the chemiluminescent intensity I_{Na} over a considerable distance range in the burned gas obeyed the flux relation (i),

$$-(k_a/A)^{1/2}\int I_{Na}\,dy = S_b(I_{Na})^{1/2} - D_H\,d(I_{Na})^{1/2}/dy,$$

$$(1)$$

which would be expected for constant sodium-atom concentration if $I_{Na} = Ak_a[H]^2$. Here, k_a is the apparent second-order recombination rate constant for a specific burned gas composition, and A is another proportionality constant; S_b is the linear burned gas velocity, while D_H is the diffusion coefficient of H atoms. This seems to us to be satisfactory evidence for reasonable constancy of the Na atom concentration, though we have not measured the latter directly.
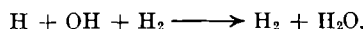
⬧

Dr. D. R. Jenkin (Shell Research Ltd., Thornton): Because of the existence of the balanced reaction

$$H_2 + OH \leftrightarrow H_2O + H,$$
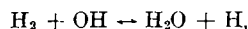
it is not possible to distinguish between the recombination reactions

$$H + H + H_2O \longrightarrow H_2 + H_2O$$

and

$$H + OH + H_2 \longrightarrow H_2 + H_2O,$$
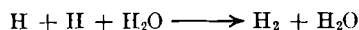
and in the equation for the rate of disappearance of H and OH in the post-reaction zone of flames, these two rate constants always appear as the sum.

I would ask Dixon-Lewis, therefore, how he is apparently able to distinguish between them and obtain individual values for them.

Dr. G. Dixon-Lewis: We agree with Jenkin that it is not generally possible to distinguish between the reactions mentioned. However, as stated by us previously, in one or two of the flames [Discussions Faraday Soc. *33*, 205 (1962)] the ratio [H]/[OH] was very high (up to 500) in the burned gas. The over-all effect in these hydrogen-rich flames was, therefore, attributed to the H-atom recombination itself.