Burning Velocity and Free Radical Recombination Rates in Low Temperature Hydrogen Flames—I. The Measurement of Temperature and Burning Velocity

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The temperatures in the range 1 300°–1 600°K of fuel-rich hydrogen–oxygen flames diluted with nitrogen, supported on a sintered metal matrix, were measured by studying the intensity of emission at 8 521 Å due to added traces of caesium. These temperatures were estimated independently from the heat of reaction and from the measured heat losses to the burner. Discrepancies of up to 100°C observed between the results of the two methods are attributed mainly to errors in the measurement of the heat loss. Adiabatic burning velocities were obtained for the same flames by extrapolation to zero heat loss. The results are in reasonable agreement with other determinations using different methods.

Introduction

IT HAS been established previously[1,2] that full thermodynamic equilibrium is not reached at the end of the reaction zone in hydrogen–oxygen–nitrogen flames, but that considerable excesses of free hydrogen atoms and hydroxyl radicals persist downstream into the burnt gases. The column of burnt gases provides a suitable isothermal system in which to study the recombination processes, which, in hydrogen-rich flames, have been shown[1] predominantly to be

$$H + H + M \longrightarrow H_2 + M \quad . \; . \; . \; . \; [1]$$

$$H + OH + M \longrightarrow H_2O + M \quad . \; . \; . \; [2]$$
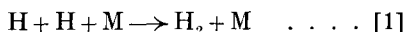
where M is a molecule of one of the bulk constituents, i.e. water, hydrogen or nitrogen. The rates of recombination have been determined in hot flames ($T > 1\,650°K$) by E. M. BULEWICZ and T. M. SUGDEN[3], who found that the apparent 'activation energy' of the rate constants varied with temperature. The present experiments were designed to extend the observations to lower temperatures in order to get further information about this effect. This first paper describes a new method of determining the temperatures in these cooler flames. A subsequent paper will deal with the rate constants.

It has been shown by P. J. PADLEY and T. M. SUGDEN[4] that the standard sodium *D*-line reversal technique[5] for measuring flame temperature breaks down below about 1 650°K in the burnt gases and 2 000°K in the reaction zone, because of chemiluminescence. For cooler flames, particularly for flat flames burnt on a sintered metal matrix, several other methods are available. W. E. KASKAN[6] has developed a technique using thermocouples, and F. J. WEINBERG and J. H. BURGOYNE[7] have measured the changes in refractive index of the flame gases to obtain temperature gradients. Both these methods, however, are more suitable for studying the detailed profile of a few flames rather than for measuring burnt gas temperatures in a large series of flames. A third method, used by D. B. SPALDING and V. S. YUMLU[8], and also by B. FINE[9], is to combine the calculated theoretical temperature with measured heat losses to the burner. Recent evidence[9,10] suggests that this method must be used with caution. Accordingly in the present series of experiments the heat loss method was compared with a spectrophotometric technique in which the intensity of a resonance line of caesium was measured.

P. J. PADLEY and T. M. SUGDEN[4] have shown that two principal mechanisms of production of electronically excited atoms X★ operate in hydrogen flame gases. The first of these is

direct collisional activation, which is balanced by the reverse quenching process,

$$X + M \rightleftharpoons X\star + M \quad \ldots \ [3]$$
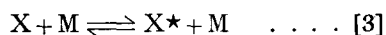
where M represents any other molecule. This is essentially a thermal equilibrium reaction and if it alone operated then $C_X\star$, and the intensity of emission under conditions of negligible self-absorption, would depend directly on exp $(-E/RT)$, where E is the energy of excitation of the upper electronic state. Then, a value of the general ambient temperature could be obtained either by a line-reversal technique, which requires rather a large amount of added metal to give sufficient contrast, or by a direct (suitably calibrated) measure of the intensity of the emission of $X\star$, in this case using a small amount of additive so as to avoid self-absorption.

The second mechanism of excitation is based on two reactions:

$$X + H + H \longrightarrow X\star + H_2 \quad \ldots \ [4]$$

$$X + H + OH \longrightarrow X\star + H_2O \quad \ldots \ [5]$$
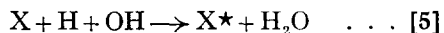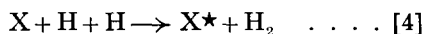
These reactions will not be balanced by the corresponding reverse reactions in most hydrogen flame gases, since the concentrations of atomic hydrogen and hydroxyl radicals in general greatly exceed those for thermodynamic equilibrium. These reactions therefore give rise to a chemiluminescent excitation and emission, which, if the reactions are exothermic, as they normally are, will not depend greatly on temperature, unlike the thermal reactions, with their exponential dependence on $(-E/RT)$.

Thus, for given E, chemiluminescence predominates at low temperatures and is gradually overtaken by thermal excitation as the temperature rises. On the other hand, at any given temperature, lines requiring large E will show chemiluminescence while lines with small E will have thermal intensities.

The flames contemplated in the present work had temperatures ranging down to about 1 300°K, and it was clear that only the resonance lines of caesium would be effectively clear of chemiluminescence under these conditions. The Cs $(^2P_{3/2} \longrightarrow ^2S_{\frac{1}{2}})$ line at 8 521 Å was selected, for which E is 33 550 cal mole^{-1}. The line

reversal technique could not be used because of blocking of the sinter burner when the necessary amount of caesium was added. Consequently, direct measurements of the intensity of emission were made with small amounts of caesium, the intensity I then being given by

$$I = A c_a \exp(-E/RT) \quad \ldots \ [6]$$

where c_a is the concentration of free metal atoms (only a very small proportion is excited) and A is an apparatus constant[12]. The method was calibrated for A by applying it to hot flames with a burner suitable for application of the sodium D-line reversal method.

Experimental

Heat loss measurements

The burner used is illustrated in *Figure 1*. The metered premixed flame gases entered the bottom chamber and flowed through the central part of the sintered brass disc. This had an overall diameter of 1 in., was 0·125 in. thick and had a mean pore size of 0·0015 in. ('Porosint' grade E). The bottom chamber was also connected to a manometer so that the pressure fall across the burner and the flame might be measured. The flame was shielded from the atmosphere by a flow of nitrogen through the middle chamber and the outer rim of the sin-
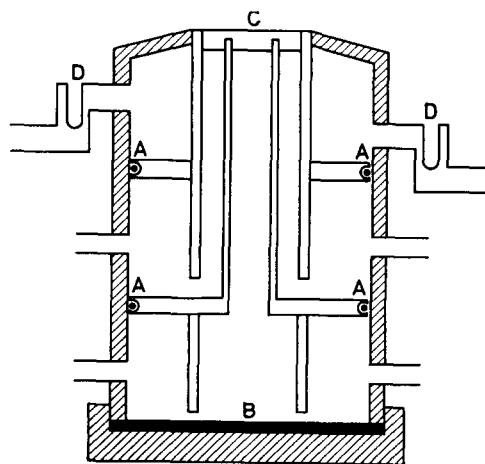

Figure 1. Sinter burner: A, Gaco ring seals; B, neoprene pad; C, brass sinter disc; D, thermocouple cups

tered disc. With the flows adjusted so that the velocities of the cold gases issuing from the two chambers were equal, the flame area was $2 \cdot 00$ cm^2, which was the same as the cross section of the inner tube. The top chamber was a water jacket. No other cooling was necessary with the flames used here. The flame gases and nitrogen shield were obtained from commercial grade cylinders, each gas being separately metered with a capillary flowmeter controlled by a needle valve. The flame gases passed through a mixing chamber before reaching the burner.

The flow of the cooling water was regulated by a constant pressure head, with a needle valve for fine control. It was measured with an inverted capillary flowmeter using the water itself as manometric fluid. Flow rates of about 100 cm^3 min^{-1} were used, giving a temperature rise of not more than 5°C when a flame was burnt. This was measured with a differential thermocouple whose junctions were placed in the leads to the cooling chamber. Dissolved air was removed from the water before passage through the burner, so that the coolant was homogeneous. For a constant flow of cooling water the heat extracted by the burner from the flame was directly proportional to the temperature rise across the cooling chamber. The sensitivity of the potentiometer and thermocouple were such that a temperature rise of $0 \cdot 005$°C could be measured.

Caesium line intensity measurement

The apparatus used was similar to that described by C. G. JAMES and T. M. SUGDEN[13]. The flame was burnt horizontally and light from a thin ($\sim 0 \cdot 15$ mm) section parallel to the burner top was focused on to the slit of a Hilger D187 constant deviation spectrometer. The light emission at $8\,521$ Å (Cs $^2P_{3/2} \rightarrow {}^2S_{\frac{1}{2}}$) was measured with an RCA 7102 photomultiplier tube. The light from the flame was chopped by a rotating sector disc at 560 c/s, and the resultant a.c. signal amplified and fed into a phase sensitive detector and demodulator. A reference square wave was generated at the same frequency using a photocell and lamp with the same sector disc. The resultant d.c. current was measured on a microammeter and was directly proportional to the intensity.

Caesium was introduced as a spray of aqueous chloride, by diverting a part of the nitrogen supply to the flame gases through an atomizer containing a $0 \cdot 001$M solution. The delivery of the atomizer was measured by comparing the intensity of emission of the Pb line at $4\,058$ Å when lead was introduced (a) as an aqueous solution of lead nitrate from the atomizer, and (b) by supplying lead tetraethyl at a known rate, based on vapour pressure data[14].

Measurement of the temperature of hot flames by the sodium D-line reversal method

The reversal technique could not be used for any flame on the sinter burner because of blocking when the salt was supplied from the atomizer in necessary quantity. Instead, therefore, a burner of the same size, in which the matrix was replaced by a bundle of stainless steel tubes of $0 \cdot 6$ mm internal diameter, was used to provide hot flames necessary for the calibration of the caesium line intensity method against the sodium D-line reversal method. Sodium was introduced into these flames from an aqueous 2M solution of the chloride in the atomizer. Reversal against a tungsten strip filament lamp was observed visually. This lamp was calibrated using an optical pyrometer standardized at the National Physical Laboratory. The detailed procedure followed is described by A. G. GAYDON and H. G. WOLFHARD[5].

Flames will be characterized here by their unburnt composition expressed (a, b), where a is the N$_2$/O$_2$ ratio, and b the H$_2$/O$_2$ ratio, by volume. The cooler flames, in which the recombination rates were investigated, had a ranging from 8 to 6 and b from $5 \cdot 03$ to $3 \cdot 5$. The hotter flames used for calibration had a ranging from 3 to 5 and b from $3 \cdot 5$ to $4 \cdot 0$, with burnt gas temperatures between $1\,700$° and $2\,080$°K. All the flames were thus hydrogen-rich.

Theoretical

The excitation of caesium

C. G. JAMES and T. M. SUGDEN[13] have studied the excitation of caesium in flames and have shown that side reactions affect the concentration of free metal atoms and hence the atomic

emission intensity. The formation of caesium hydroxide (CsOH) and caesium ions (Cs⁺) (the latter particularly in hot flames) reduces the concentration of free metal atoms. Corrections for these effects must be made if a comparison of the observed intensities under varying conditions is to be used to obtain temperatures.

The total caesium in the flame gases can be expressed as an effective concentration c_t, which is the sum of three terms

$$c_t = c_a + c_h + c_i \qquad \cdots \cdot [7]$$

where c_a, c_h, c_i respectively are the concentrations of Cs atoms, CsOH molecules and Cs⁺ ions. Defining $\phi \equiv c_h/c_a$ and $x \equiv c_i/c_t$,

$$c_a = (1-x)\, c_t/(1+\phi) \qquad \cdots \cdot [8]$$

and the intensity I of the emission line under conditions of negligible self-absorption is

$$I = Ac_a \exp(-33\,550/RT) \qquad \cdots [9]$$

since the excitation energy of the resonance $^2P_{3/2}$ level of caesium is 33 550 cal mole⁻¹; A is a constant of the apparatus, but includes the transition probability. Hence if the system can be calibrated for known c_a at known temperatures, it will be possible to obtain temperatures for other flames in which c_a (or its value relative to the calibrating values) is known.

The value of ϕ is governed by the balanced reaction

$$Cs + H_2O \rightleftharpoons CsOH + H \quad \cdots [10]$$

with equilibrium constant

$$K = c_h c_H / c_{H_2O} c_a = \phi c_H / c_{H_2O} \cdots [11]$$

K has been obtained by C. G. James and T. M. Sugden[13]; c_{H_2O} is readily found from the burnt gas composition, and c_H can be measured by spectrophotometric means[15]. Hence ϕ can be evaluated. As c_H decreases downstream ϕ increases and therefore the intensity of emission decreases. Values of ϕ in the region of unity were found for the calibration flames, but for the cooler, experimental flames the constant emission downstream, as shown in *Figure 2*, indicated that for them ϕ was negligible compared with unity.
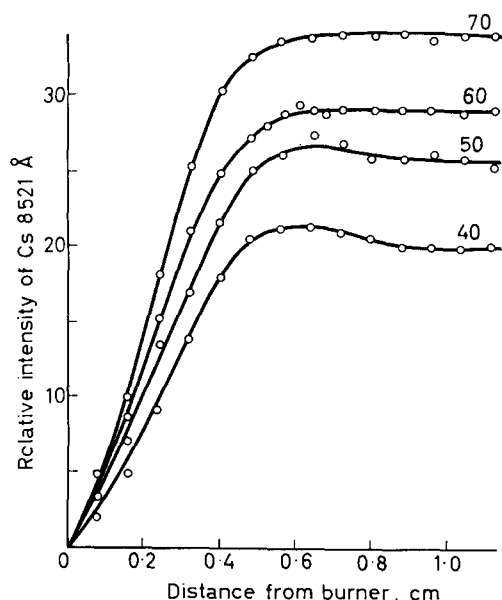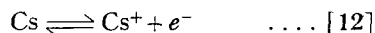

Figure 2. Plots of emission intensity of Cs 8521 Å *line for a set of flames with a* $(N_2/O_2)=8\cdot0$, b $(H_2/O_2)=4\cdot5$. *The (cold) gas velocity* $(V \text{ cm sec}^{-1})$ *in the burner is indicated on the curves*

The value of x is governed by the equilibrium[16]

$$Cs \rightleftharpoons Cs^+ + e^- \qquad \cdots [12]$$

with equilibrium constant

$$K_+ = c_i^2/c_a \qquad \cdots \cdot [13]$$

on the basis of caesium ions and electrons as the only charged particles in significant concentrations. This leads to a value of x

$$x = \frac{K_+}{2c_t\,(1+\phi)} \left\{ -1 + \left(\frac{1 \pm 4c_t\,(1+\phi)}{K_+} \right)^{\frac{1}{2}} \right\} . \; [14]$$

K_+ being obtained from the thermodynamic equation of Saha

$$\log K_+ = -5\,050V/T + (5/2) \log T - 6\cdot49 . \; [15]$$

in which V is the ionization potential in electron volts (3·89 eV for caesium), T is the absolute temperature in °K, and K_+ is in atmospheres. Ionization was negligible for the cool, experimental flames, but a significant correction had to be made for the calibrating flames.

Since caesium salt was supplied to the unburnt gases at a constant rate, then further, readily calculable corrections had to be made to obtain the relative total concentration c_t in various flames because of the different changes in volume on burning, and different final temperatures.

Temperatures based on heat loss measurements
The heat loss to the burner expressed (for fuel-rich flames) as S calories per mole of oxygen passing through the burner, is related to the measured temperature rise of ΔT across the burner by

$$S = \Delta T \, (c_w m_w + c_g m_g) / \alpha B \quad \cdots \quad [16]$$

where m_w and m_g are the mass of water and gas (including the nitrogen shield) passing through the burner per second and c_w and c_g are the specific heats of the water and gas respectively. α is the molar volume fraction of oxygen (mole O_2 cm^{-3}) in the initial mixture and B is the volume rate of flow of cold gas (cm^3 sec^{-1}). The term $c_g m_g$ is small compared with $c_w m_w$.

For a given composition it is possible to obtain the adiabatic enthalpy change from the overall heat of reaction and tables of enthalpy content[17], on condition that the burnt gas composition is known or assumed. In the present work on hydrogen-rich flames the burnt gases have been assumed to contain only water, nitrogen and the excess hydrogen. No allowance has been made for dissociation, incomplete combustion or secondary combustion at the edges of the flame. The first two are entirely reasonable for the rather cool flames used. The final one is permissible since a nitrogen shield was used.

To obtain the enthalpy change (and hence the temperature) in the flame subject to heat losses, it must be assumed that S is the only loss suffered by the flame. This is clearly only approximately true, since losses to the atmosphere by convection and radiation must also occur; the latter may amount to as much as 10 to 20 per cent of the heat of reaction[5]. In the present paper the enthalpy changes in flames subject to heat loss were obtained by subtracting

the measured value of S from the heat of reaction (115·6 kcal mole^{-1} of oxygen).

Results and Discussion

Temperature
The detailed temperatures of the individual flames burnt, ranging from 1 300° to 1 600°K are of interest only for the purpose of Part II of this paper but a comparison of the two methods used is of more general interest. *Figure 3* shows plots of log v against $1/T_b$ for four flame gas compositions, where v is the burning velocity, obtained directly from V, the gas velocity in the burner, with a small correction (<1 per cent) for the pressure drop across the matrix. Good straight lines are obtained, confirming the results of W. E. KASKAN[18], but the heat loss temperatures for a given composition generally fall on different lines from the photometric values. The maximum deviation is about 100°C for the leanest flame ($b = 3·5$) burnt at the slowest speed ($V = 40$ cm sec^{-1}).

It may be observed from *Figure 3* that the heat loss temperature is generally higher than the photometric one, the difference decreasing
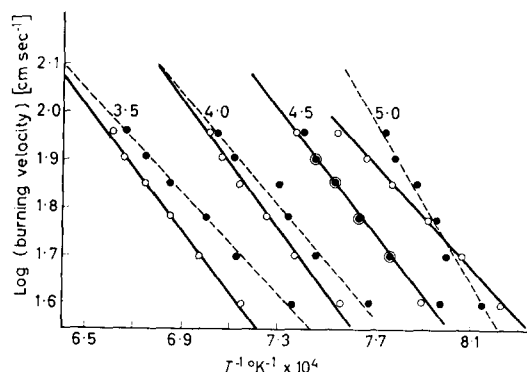

Figure 3. Plots of log *(burning velocity)*, [V cm sec^{-1}], *against* $1/T$ *for a set of flames with a* ($N_2/O_2 = 8·0$) *and various* b (H_2/O_2) *ranging from 3·5 to 5·0 as indicated. Open points and full lines represent the results of the heat-loss method. Filled points and broken lines represent the results of the caesium intensity method. The* $b = 4·5$ *lines are coincident, as are many of the points on them. The abscissae* (T^{-1}) *axis is as shown for* $b = 3·5$. *For* $b = 4·0$, $4·5$, $5·0$ *the lines have been moved successively* $0·4°K^{-1} \times 10^4$ *to the right for clarity*

with decreasing flame speed and increasing hydrogen content of the burnt gases, except for the richest flames where the heat loss temperatures are lower than the photometric ones at the higher speeds.

It is believed that the discrepancies between the two methods arise largely from systematic errors in the heat loss method, rather than in the spectrophotometric one. Radiation losses have been neglected in the heat loss method. A loss of ten per cent of the heat of reaction in this way will result in the quoted heat loss temperatures being about 100°C too high. This effect will increase with temperature at any given flame speed. In addition, secondary combustion of the excess hydrogen with entrained air will tend to be greater the richer the flame mixture. This will increase the measured heat loss and hence cause the heat loss temperature to be low. Combustion of 0·1 mole of excess hydrogen per mole of flame gas corresponds to about 50°K in the calculated temperature. The coincidence of the results of the two methods for the flame (8; 4·0), (Figure 3), is thus probably fortuitous, the two effects cancelling out. In richer flames the secondary combustion is expected to be of greater importance than the unmeasured heat losses, while in the other flames the latter should predominate, in agreement with the tendencies shown in Figure 3.

That v should depend exponentially on temperature is to be expected from a consideration of most flame propagation theories, which predict a relation between the adiabatic burning velocity v_a and the mean rate of reaction U_m in the flame front of the kind[5]

$$v_a{}^2 = CU_m \qquad \ldots \ldots [17]$$

where C is a complicated parameter of the flame gases, changing only slowly with temperature in comparison with U_m. Since reaction rates are generally exponential functions of temperature, a plot of log v_a against $1/T_m$ should be a straight line. In so far as cooling a flame has little effect on C, such a relationship should also hold for cooled flames. The slope of such a line yields the apparent activation energy of the reaction rate. It is important, however, not to

assume that these will be the same as the energy of activation associated with a rate constant, since the mean concentrations of reactants in the reaction zone may also vary rapidly with temperature, especially where free radicals are concerned.

For a set of flames, such as those shown in Figure 3, for which the composition only changes a little from flame to flame it may be expected that the apparent activation energy of the reaction rate (i.e. the slope of log v against $1/T_b$) will be approximately constant. The lines obtained from the spectrophotometric measurements agree with this hypothesis, whereas those obtained from the heat loss method vary systematically. This is considered to be further confirmatory evidence that the spectrophotometric method is less subject to systematic error. (It is important in this connection to remember that the lines in Figure 3 are staggered along the temperature axis.) In reality they are much closer together, so that the temperature in the four flames at any given speed is roughly the same.) The apparent activation energy of U_m obtained from the spectrophotometric measurements is about 53 ± 6 kcal mole^{-1} for the flames shown in Figure 3.

Adiabatic burning velocity

The burning velocities of the adiabatic flames were obtained by plotting log v against S, when straight lines were obtained (Figure 4). This is
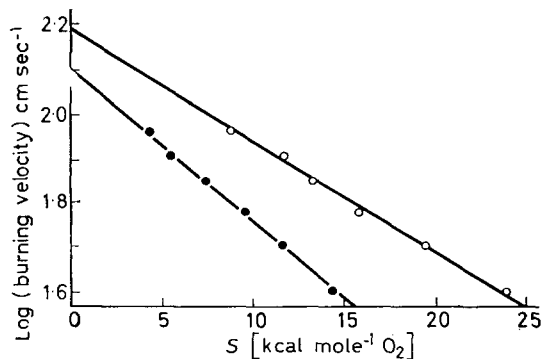
Figure 4. Typical linear extrapolations of log (burning velocity), [V cm sec^{-1}] against heat loss S (kcal mole^{-1} O$_2$). Open points for flame a=6·0, b=3·5; filled points for flame a=8·0, b=4·5

expected since in the range of temperatures considered, $1/T_b$ is nearly linearly related to $(T_{adiabatic} - T_b)$, which in turn is directly proportional to S, since the specific heat of the burnt gases changes only slowly with temperature for a given composition. Extrapolation to $S = 0$ yields the adiabatic burning velocity for flames with initial gas temperature near $300°K$, subject to the normal radiation losses encountered in the laboratory. The results obtained are therefore directly comparable with those found in the literature (G. JAHN[19], E. BARTHOLOMÉ[20], D. A. SENIOR[21]). They are shown in *Table 1*. In

Table 1. Adiabatic burning velocity in cm sec^{-1} as a function of composition $a = N_2/O_2$, $b = H_2/O_2$ by volume: (i) this work, (ii) G. JAHN[19]

b	Source	$a=8$	7	6	5
5·0	(i)	124	126	146	—
	(ii)	75	90	105	—
4·5	(i)	129	132	150	—
	(ii)	95	110	135	—
4·0	(i)	132	136	155	239
	(ii)	95	115	140	120
3·5	(i)	131	137	157	—
	(ii)	90	115	145	—
3·0	(i)	—	—	156	—
	(ii)	75	100	140	—

general the values found here are 15 to 40 per cent higher than those of Jahn. Bartholomé's results for less dilute flames were also about 40 per cent higher than Jahn's. Senior reported agreement with Bartholomé on the hydrogen-rich side of stoichiometry and with Jahn on the hydrogen-lean side. Jahn's values might be expected to be low because he used the luminous cone of a bunsen flame, which tends to overestimate the area of the flame front.

Conclusions

A spectrophotometric technique based on the thermal emission of controlled traces of added caesium has been developed for measuring low flame temperatures. The effects of compound formation and ionization on the observed intensity appear to be negligible below $1600°K$ at least for fuel-rich flames. The method is limited towards lower temperatures by the thermal excitation giving way to predominantly chemilu-

minescent effects. At $1300°K$ this effect was just visible in the reaction zone (see *Figure 2*) but in the burnt gases, where free radical concentrations, and hence chemiluminescence, are lower, it should be possible to use the method down to temperatures not much above $1000°K$. It has been confirmed that the estimation of temperature from measured heat losses is unreliable.

Values of adiabatic burning velocities have been presented which are in substantial agreement with previous determinations using other methods.

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Burning Velocity and Free Radical Recombination Rates in Low Temperature Hydrogen Flames —II. Rate Constants for Recombination Reactions

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The chemiluminescence of atomic lead has been used to measure concentrations of atomic hydrogen and hydroxyl radicals in premixed flames of hydrogen, oxygen and nitrogen at atmospheric pressure over the temperature range 1 300°–1 600°K. A suitable calibration was made against the absolute sodium–lithium method by using flames at higher temperatures. The results were used to evaluate ternary rate constants for the reactions

$$H + H + M \xrightarrow{k_H^M} H_2 + M$$

$$H + OH + M \xrightarrow{k_{OH}^M} H_2O + M$$
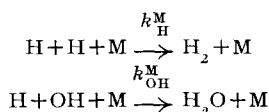
The following values were obtained for 1400°K, with no measurable temperature variation over the range studied:

$$k_{H_2}^{H_2} = 4 \cdot 8 \times 10^{-32}, \quad k_H^{N_2} = 2 \times 10^{-33}, \quad k_{OH}^{H_2O} = 2 \cdot 8 \times 10^{-31},$$

$$k_{OH}^{N_2} = 1 \cdot 8 \times 10^{-31} \ cm^6 \ molecule^{-2} \ sec^{-1}.$$

Introduction

IT IS well established that atomic hydrogen and hydroxyl radicals are produced in the reaction zones of hydrogen–oxygen–nitrogen flames in amounts which may greatly exceed those for thermodynamic equilibrium[1,2]. The recombination of these free radicals towards equilibrium occurs predominantly by the reactions 1 and 2:
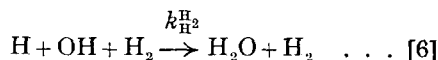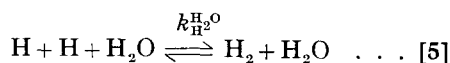
$$H + H + M \xrightarrow{k_H^M} H_2 + M \quad \ldots \ldots [1]$$

$$H + OH + M \xrightarrow{k_{OH}^M} H_2O + M \quad \ldots \ldots [2]$$
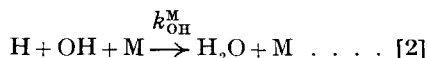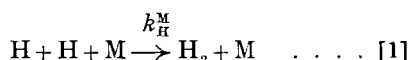
where M is any third body. In fuel-rich flames the bulk of molecules M will be either H_2, H_2O, or N_2, so that six ternary rate constants are concerned. A number of previous researches have been concerned with the determination of these rate constants[3–5], but much more information is required for completeness. It might be thought

that all six constants could be deduced from experiments involving isothermal variation of the burnt gas composition. In fact, only five independent pieces of information can be obtained since there is a rapid, reversible bimolecular reaction, shown in equation 3, which occurs at such a rate that the concentrations C_{H_2}, C_{H_2O}, C_H and C_{OH} are linked by equation 4.

$$H_2O + H \rightleftharpoons H_2 + OH; \ eqn \ const. \ K_O \quad \ldots \ldots [3]$$
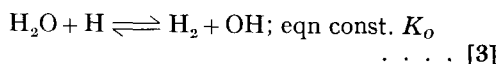
$$\frac{C_{H_2} \times C_{OH}}{C_{H_2O} \times C_H} = K_O \quad \ldots \ldots [4]$$

In consequence, the effects of the reactions

$$H + H + H_2O \underset{}{\overset{k_H^{H_2O}}{\rightleftharpoons}} H_2 + H_2O \quad \ldots [5]$$

$$H + OH + H_2 \xrightarrow{k_{OH}^{H_2}} H_2O + H_2 \quad \ldots [6]$$

cannot be distinguished from one another. The

total rate of disappearance of free radicals is

$$-\frac{\mathrm{d}[C_H + C_{OH}]}{\mathrm{d}t} = \sum_M [k^M C^2 + 2k^M_{OH} C_H C_{OH}] C_M$$

$$\cdots \text{[7]}$$

Writing, from 4,

$$C_{OH} = \frac{C_{H_2O}}{C_{H_2}} K_O C_H \equiv \alpha C_H \quad \cdots \text{[8]}$$

we have

$$\frac{\mathrm{d}C_H}{\mathrm{d}t} = \frac{C_H^2}{(1+\alpha)} \sum_M [k^M_H + 2\alpha k^M_{OH}] C_M \quad \cdots \text{[9]}$$

where M is H_2, H_2O, or N_2 (fuel-rich flames). Writing the summation simply as $\overline{kM}$, this becomes

$$-\frac{\mathrm{d}C_H}{\mathrm{d}t} = \frac{\overline{kM}}{(1+\alpha)} C_H^2 \quad \cdots \text{[10]}$$

which on integration gives

$$\frac{1}{C_{H(2)}} - \frac{1}{C_{H(1)}} = \frac{\overline{kM}}{(1+\alpha)} (t_2 - t_1) \quad \cdot \text{[11]}$$

The object of the present work is to obtain $\overline{kM}$ from measurements of C_H as a function of time. The quantity α is well known from tabulations of the equilibrium constant K_O combined with the concentrations C_{H_2} and C_{H_2O}, which are both large in sufficiently fuel-rich flames.

Experimental

Fuel-rich flames of premixed hydrogen, oxygen and nitrogen were obtained at atmospheric pressure using a sintered burner to give flat reaction zones as described in Part I[6]. Small amounts of additives were fed to the central region of the flame supply, the rest of the flame acting as an annular shield for a few centimetres above the burner. The principal additive here was the vapour of lead tetraethyl, obtained by passing a stream of nitrogen through a thermostatically controlled saturator containing the liquid lead compound. Amounts of this vapour were used which gave about one part of atomic lead to 10^5 parts of burnt flame gases. Lead tetraethyl is completely decomposed in the reaction zone to give atomic lead, which then produces

a chemiluminescence in the flame gases related to the concentrations of the free radicals H and OH[7].

This method of obtaining free radical concentrations is a relative one only, and was used because the addition of lead could be made in vapour form. The absolute method based on the relative intensities of the resonance radiation of sodium and lithium additives[1] could not be used for two reasons—because the method requires thermal excitation of the resonance lines, whereas the temperatures used here (1 300°–1 600°K) were so low as to give predominantly chemiluminescence, and because the sinter always tends to become clogged when aqueous sprays of salt solutions are used. Hence a calibration was made as follows. Eight flames were burnt on a Meker type of burner, made of a bundle of fine hypodermic tubes, as described previously[6]. These flames were sufficiently hot to give predominantly thermal excitation of sodium and lithium, and hence to allow use of the absolute method for estimation of C_H. Lead tetra-ethyl was also added as vapour under the same conditions as those used with the sintered burner. The diameter of the coloured central column of flame gases was the same for the two burners.

The optical arrangements for measuring the intensity of the light emitted from narrow parts of the visible or ultra-violet spectrum was as described in Part I[6], except that a 1P21 photomultiplier was used, rather than an infra-red sensitive one. Series of flames of given bulk composition, but different temperatures, were obtained as previously described by adjusting the rates of flow to correspond with a range of burning velocities. Use of the resonance radiation of caesium to measure flame temperatures in the region 1 300°–1 600°K has also been described in Part I[6].

Results
'High temperature' calibration flames
Absolute values of C_H were obtained by the lithium–sodium method developed by E. M. Bulewicz, C. G. James and T. M. Sugden[1]. When these metals are excited thermally in flame gases the relative intensities of their

resonance lines can be used to give a quantity ϕ, defined by

$$\phi = (C_{H_2O}/C_H) K_{Li} \qquad \ldots \ldots [12]$$

where K_{Li} is the equilibrium constant of the reaction

$$Li + H_2O = LiOH + H \qquad \ldots \ldots [13]$$
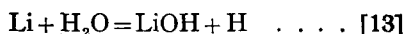
L. F. PHILLIPS[8] has obtained reliable values of K_{Li} at temperatures in the range of $2\,400°$–$2\,700°K$ by use of flames in which C_H takes its equilibrium value. These can be extrapolated to lower temperatures with confidence. A typical plot of $1/C_H$ against distance from the

reaction zone is shown in *Figure 1*(a) for a 'calibration' flame. It is a good straight line, as expected from equation 11.

P. J. PADLEY and T. M. SUGDEN[7] have shown that lead gives chemiluminescent emission at $4\,058\,Å$ in flames such as this with an intensity I_{Pb} which is proportional to $C_H \times C_{OH}$ and hence to αC_H^2. Since α is nearly constant in the burnt gases of a fuel-rich flame then $I_{Pb}^{\frac{1}{2}}$ should give a straight line through the origin when plotted against C_H, determined at various points by the sodium–lithium method. This is shown in *Figure 1*(b).

Data for all eight calibration flames are shown in *Table 1*.
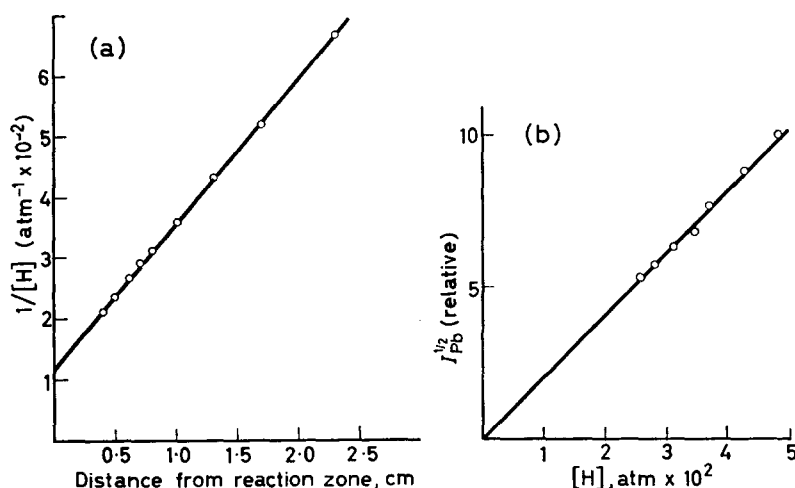
Figure 1. (a) *Plot showing the bimolecular decrease of concentration of atomic hydrogen,* [H], *away from the reaction zone of a typical flame:* (b) *linear dependence of the square root of the chemiluminescent emission of Pb (4058 Å) on* [H]

Table 1.   Results for high temperature calibration flames

Flame		$(1/C_H)$ slope $(cm^3$ molecule^{-1} sec$^{-1} \times 10^{14})$	$(1/C_H)$ intercept $(cm^3$ molecule$^{-1} \times 10^{17})$	$(1/C_H)$ plots $\left(\dfrac{slope}{intercept}\right) \times 10^{-3}$	$1/I_{Pb}^{\frac{1}{2}}$ slope (sec^{-1} $\times 10^2$)	$1/I_{Pb}^{\frac{1}{2}}$ intercept $\times 10^2$	$1/I_{Pb}^{\frac{1}{2}}$ plots $\left(\dfrac{slope}{intercept}\right) \times 10^{-3}$	$T°K$
a, (N$_2$/O$_2$)	b, (H$_2$/O$_2$)							
2·96	3·55	7·50	1·41	5·3	0·96	1·81	5·3	2 079
3·00	4·00	7·44	1·81	4·1	1·19	2·90	4·1	1 945
3·00	4·50	7·23	2·67	2·7	1·17	4·35	2·7	1 877
4·00	4·00	9·66	1·89	5·1	1·42	2·74	5·2	1 796
5·00	3·50	10·15	2·60	3·9	1·80	4·72	3·8	1 770
4·74	3·86	9·10	2·85	3·2	1·93	5·85	3 3	1 763
5·00	4·00	8·99	2·72	3·3	1·72	5·30	3·3	1 702
6·00	3·50	9·05	3·48	2·6	1·81	6·70	2·7	1 682

Flames are characterized by two quantities a and b, which give the volume ratios N_2/O_2 and H_2/O_2 respectively in the unburnt gases. Plots of $1/C_H$ against t were made for each flame, conversion from distance to time being made from the known rate of flow of the burnt gases. Similarly, plots of $1/I_{Pb}^{\frac{1}{2}}$ against time were made. *Table 1* quotes both the slopes and ordinate intercepts of these plots—in cm^3 molecule^{-1} units for C_H and arbitrary units for I_{Pb}. That the two types of plot are essentially similar

observed as a function of distance from the reaction zone in low temperature flames on the sinter burner. The parameter a was taken as 8·0, 7·0 and 6·0, and each of these values used with b equal to 5·0, 4·5, 4·0 and 3·5. Each flame was burnt at six speeds, giving a total of 72 flames, with temperatures ranging from 1 300° to 1 600°K, as set out in the previous paper[6]. Plots of $1/I_{Pb}^{\frac{1}{2}}$ against time were good straight lines, resembling *Figure 1*(a). Using *Figure 2* as a basis for calibration, values of
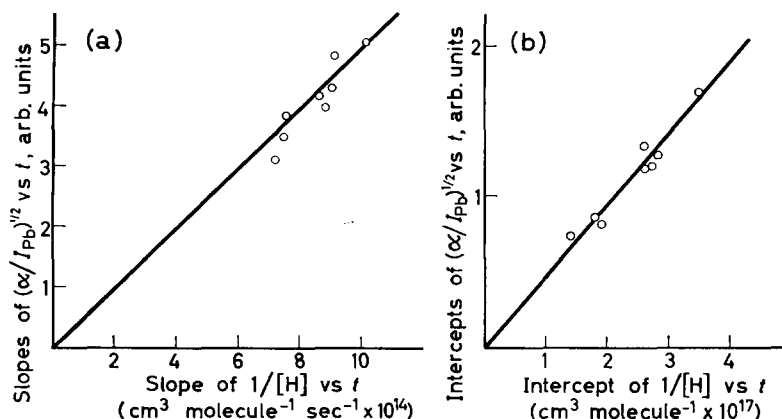

Figure 2. Calibration of lead chemiluminescence based on (a) *slopes of recombination curves:* (b) *intercepts of recombination curves*

is shown by the excellent agreement of the two (slope / intercept) columns.

The chemiluminescent intensity I_{Pb} is equal to $C_H C_{OH}$, or αC_H^2, multiplied by some constant. Hence the slope of plots of $(\alpha/I_{Pb})^{\frac{1}{2}}$ against t, when plotted against the slope of plots of $1/C_H$ against t, should yield a straight line passing through the origin. Such a line is shown in *Figure 2*(a). It is not altogether satisfactory because of the small spread of the points and their remoteness from the origin. *Figure 2*(b), in which intercepts have been substituted for slopes, is a much more convincing correlation, and lends strong support to the use of *Figure 2*(a) in providing a conversion factor from slopes of $(1/I_{Pb}^{\frac{1}{2}})$ against t to slopes of $(1/C_H)$ against t.

Low temperature flames

The chemiluminescence of lead (4 058 Å) was

the slope of $1/C_H$ against time were deduced. These are equal to $\overline{kM}/(1+\alpha)$ from equation 11, and were converted to $\overline{kM}$. The factor $(1+\alpha)$ ranged from 1·02 to 1·05. *Figure 3* shows a typical plot of $\overline{kM}$ against temperature for a specimen flame, higher temperatures corresponding generally with higher burning velocities.

The tendency of $\overline{kM}$ to increase with temperature for a given flame composition is at first sight anomalous, since ternary rate constants as a rule show a slow decrease with increasing temperature. The reason for the observed effect, however, lies in the term in α in $\overline{kM}$ (equation 9). This increases with increasing temperature because K_0 does so (from $1·4 \times 10^{-2}$ at 1 300°K to $4·0 \times 10^{-2}$ at 1 600°K). This means that C_{OH} will rise quite rapidly and that recombination involving k^M_{OH} becomes relatively more

important at higher temperatures. From plots like that of *Figure 3*, values of $\overline{kM}$ have been
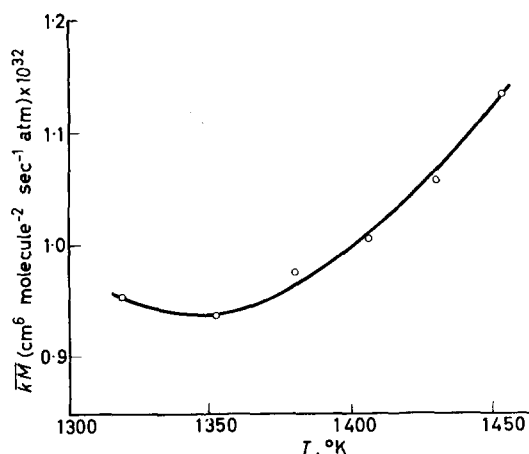
Figure 3. $\overline{kM}$ *against T for a flame with* $a = 7 \cdot 0$, $b = 5 \cdot 0$

interpolated for various compositions at temperatures of $1\,350°$, $1\,400°$, $1\,450°$ and $1\,500°$K, and are shown in *Table 2*.

gases is one atmosphere, and is made up of the partial pressures of the species H_2, H_2O and N_2. These partial pressures are:

$$p_{H_2O} = 2/(a+b)$$
$$p_{N_2} = a/(a+b) \qquad \left.\right\} \quad \dots \ [14]$$
$$p_{H_2} = (b-2)/(a+b)$$

all in atmospheres. Multiplying $\overline{kM}$ by $(a+b)$ and expanding

$$\overline{kM}(a+b) = k_{H^2}^{H_2}(b-2) + 2k_{H^2}^{H_2O} + 4K_o k_{OH^2}^{H_2}$$
$$+ \frac{8K_o}{(b-2)} k_{OH^2}^{H_2O} + k_{H^2}^{N_2} + \frac{4aK_o}{(b-2)} k_{OH^2}^{N_2} \quad \dots \ [15]$$

Hence, for given temperature and b, plots of $\overline{kM}(a+b)$ against a should be straight lines of slope $[k_{H^2}^{N_2} + 4K_o k_{OH^2}^{N_2}/(b-2)]$ and intercept equal to the sum of the first four terms of the RHS of equation 15. Such plots are shown in *Figure 4*, for mean temperatures of $1\,400°$K, obtained by averaging the values of $\overline{kM}(a+b)$ at $1\,350°$, $1\,400°$ and $1\,450°$K.

Table 2. Values of $\overline{kM}$ *in* cm^6 *molecule*$^{-2}$ sec^{-1} $atm \times 10^{32}$

$a=(N_2/O_2)$	$b=(H_2/O_2)$	1 350	1 400	1 450	1 500
8·0	5·0	0·905	0·965	1·075	—
	4·5	0·970	1·020	1·120	—
	4·0	1·015	1·092	1·205	—
	3·5	1·140	1·265	1·410	1·565
7·0	5·0	0·940	1·000	1·125	—
	4·5	0·995	1·055	1·140	—
	4·0	1·060	1·110	1·220	1·370
	3·5	—	1·320	1·465	1·370
6·0	5·0	0·965	1·025	1·115	1·200
	4·5	1·040	1·100	1·180	1·280
	4·0	1·075	1·130	1·235	1·405
	3·5	—	1·350	1·500	1·730

(The column header row above reads: $T°K$ spanning 1 350 / 1 400 / 1 450 / 1 500)

All values of $\overline{kM}$ are given here in units of cm^6 molecule^{-2} sec^{-1} atm, obtained by dividing the values obtained from the plots, in units of cm^3 molecule^{-1} sec^{-1} by the number of molecules per cm^3 at the appropriate temperature.

Discussion

Evaluation of rate constants

In the unburnt gases $(C_{N_2}/C_{O_2}) = a$, and $(C_{H_2}/C_{O_2}) = b$. The total pressure of the burnt

This procedure may be justified as follows: three points is the minimum number through which a straight line may reasonably be drawn, and if these are obtained by statistical averaging they should be more accurate. The quantity $\overline{kM}(a+b)$ is found to rise linearly with increasing temperature over the range $1\,350°$–$1\,450°$K within experimental error, and therefore simple averaging is justified. It is realized that this procedure precludes use of the data for extract-
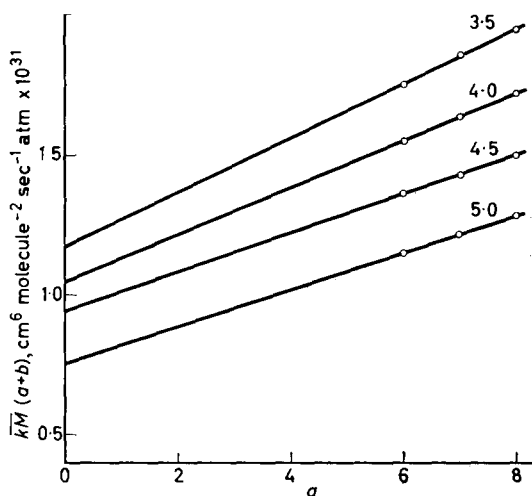
Figure 4. $\overline{kM}\,(a+b)$ against a for flames of various b shown by the numerals on the various lines

ing variations of the rate constants. On this basis *Figure 4* shows good straight lines, of slope increasing with decreasing b. Plotting these slopes against $[2/(b-2)]$ yields the line of *Figure 5*. The slope of this line is $2K_o k_{OH^2}^{N^2}$, and the intercept on the ordinate axis is $k_{H^2}^{N^2}$, and hence the two rate constants at $1\,400°K$ are determined. They are:

$$k_{H^2}^{N^2} = 2 \times 10^{-33}\;\text{cm}^6\,\text{molecule}^{-2}\,\text{sec}^{-1}$$

$$k_{OH^2}^{N^2} = 1\cdot3 \times 10^{-31}\;\text{cm}^6\,\text{molecule}^{-2}\,\text{sec}^{-1}$$

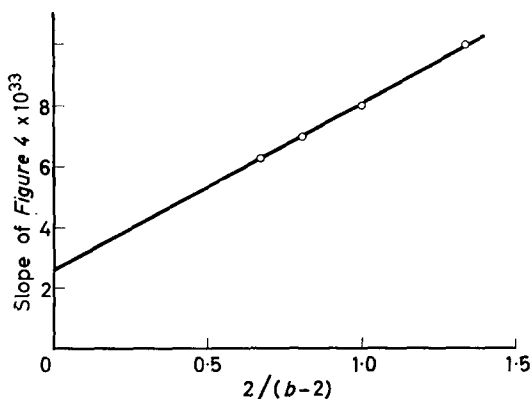*Figure 5. Plot for determination of $k_{OH}^{N_2}$ and $k_H^{N_2}$*

The intercepts of *Figure 4* yield average values of the function

$$k_{H^2}^{H^2}\,(b-2) + [\,2k_{H^2}^{H^2O} + 4K_o k_{OH^2}^{H^2}\,]$$

$$+ \frac{8K_o}{(b-2)}\;k_{OH^2}^{H^2O} \quad \cdots \;[16]$$

Sets of three simultaneous equations in $k_{H^2}^{H^2}$, $(2k_{H^2}^{H^2O} + 4K_o k_{OH^2}^{H^2})$, and $8K_o k_{OH^2}^{H^2O}$ are obtained, which can be solved to give these quantities. The solutions yield:

$$k_{H^2}^{H^2} = 4\cdot8 \times 10^{-32}\;\text{cm}^6\,\text{molecule}^{-2}\,\text{sec}^{-1}$$

$$k_{OH^2}^{H^2O} = 2\cdot8 \times 10^{-31}\;\text{cm}^6\,\text{molecule}^{-2}\,\text{sec}^{-1}$$

$$k_{H^2}^{H^2O} + 2K_o k_{OH^2}^{H^2} = 2\cdot0 \times 10^{-32}\;\text{cm}^6\,\text{molecule}^{-2}\,\text{sec}^{-1}$$

all at $1\,400°K$, with $K_o = 0\cdot021$. Errors on k_{H^2} and k_{OH^2} are estimated at ± 30 per cent, and on $k_{H^2}^{H^2}$ and $k_{OH^2}^{H^2O}$ at ± 50 per cent.

Comparison with previous results

Previous results are available from E. M. BULE-WICZ and T. M. SUGDEN[3] at $1\,650°K$, and from G. DIXON-LEWIS, M. M. SUTTON and A. WILLIAMS[5] at $1\,078°K$, all obtained with hydrogen flames. They are shown, together with the present ones, in *Table 3*.

Table 3. Comparison with previous results

Rate constant	Dixon-Lewis, Sutton and Williams[5] 1 078°K	Present work 1 400°K	Bulewicz and Sugden[3] 1 650°K
$k_H^{H_2}$	$1\cdot7 \times 10^{-32}$	$4\cdot8 \times 10^{-32}$	—
$k_H^{H_2O}$	1×10^{-32}	2×10^{-32}	6×10^{-32}
$k_H^{N_2}$	1×10^{-32}	3×10^{-33}	—
$k_{OH}^{H_2}$	—	1×10^{-30}	—
$k_{OH}^{H_2O}$	$2\cdot5 \times 10^{-31}$	$2\cdot8 \times 10^{-31}$	$1\cdot5 \times 10^{-30}$
$k_{OH}^{N_2}$	$2\cdot5 \times 10^{-31}$	$1\cdot3 \times 10^{-31}$	—

The results of Bulewicz and Sugden can be neglected here, since they were based on the assumption that only H_2O molecules were effective as third bodies, an assumption now shown to be unwarranted. The values of k_H at $1\,078°K$ and $1\,400°K$ may be compared directly, while those of Dixon-Lewis *et al.* for k_{OH} must be divided by two for purposes of com-

parison, on account of differences of defini-
tion. Dixon-Lewis *et al.* separated $k_{H_2O}^{H}$ from
$k_{OH}^{H_2}$ by assuming $k_{H_2O}^{H} = k_{H}^{N_2}$, obtaining a value
for $k_{H_2O}^{H}$ a result not inconsistent with the present
work.

On the basis that the temperature variation
is small, as would seem reasonable since a
'negative energy of activation' of 3 kcal would
reduce a rate constant only to 70 per cent of its
value at $1\,078°K$ in going to $1\,400°K$, the two
sets of results are not completely inconsistent,
bearing in mind the errors involved—both ex-
perimentally in the measurement of concentra-
tion of radicals, and in the evaluation of the
separate constants from the overall results. Per-
haps the best comparison is to be made on the
overall results at this stage. For a flame with
approximate composition 8 N_2 : 1 H_2O : 1 H_2 at
$1\,072°K$ Dixon-Lewis *et al.* obtain an effective
overall second-order rate constant (i.e. one in-
cluding concentrations of third bodies) of 4.7×10^{10} cm^3 mole^{-1} sec^{-1}. The nearest flame to
this in the present work was 8 N_2 : 2 H_2O : 1·5
H_2 at $1\,309°K$, which gave a corresponding
value of 3.0×10^{10} cm^3 mole^{-1} sec^{-1}. Such
agreement is very satisfactory.

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