RADICAL RECOMBINATION REACTIONS IN $H_2/O_2/N_2$ FLAMES: PARTICIPATION OF THE HO_2 RADICAL

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Radical recombination rates have been measured in fuel-lean $H_2/O_2/N_2$ flames at temperatures up to $2130°K$. The observed rates cannot be accounted for in terms of termolecular reactions such as $H + OH + M \to H_2O + M$ and the occurrence of an additional recombination route, $H + O_2 + M \overset{5}{\rightleftharpoons} HO_2 + M$, $HO_2 + OH \overset{7}{\to} H_2O + O_2$, satisfies the experimental results. A value for k_7 of 1.2×10^{13} cm^3 $mole^{-1}$ sec^{-1} at $2130°K$ is derived.

1. Introduction

An important feature of the structure of flames is the presence of free radicals in the post-reaction zone in concentrations often considerably higher than their thermal equilibrium values [1]. This is a consequence of rapid bimolecular reactions such as:

$$H + O_2 \rightleftharpoons OH + O \tag{1}$$

and

$$O + H_2 \rightleftharpoons OH + H \tag{2}$$

occurring in the flame front, together with the slowness of termolecular reactions such as:

$$H + H + M \to H_2 + M , \tag{3}$$

$$H + OH + M \to H_2O + M . \tag{4}$$

Studies of the decay of radicals in the burnt gas downstream from the flame front in fuel-rich hydrogen/oxygen/nitrogen flames have led to values for the rate constants of reactions (3) and (4) for a variety of third bodies, M, (e.g., ref. [2]) which complement data obtained by other techniques [3].

In fuel-lean $H_2/O_2/N_2$ flames it appears that the observed recombination rates cannot be satisfactorily accounted for in terms of three-body recombination reactions such as (3) and (4). Thus, work by Kaskan [4], Fenimore and Jones [5] and Dixon-Lewis et al.

[6] with flames and by Getzinger and Schott [7] with shock-heated H_2/O_2 mixtures has demonstrated that, at temperatures up to $1500°K$ at least, an additional recombination route may be via the reaction sequence,

$$H + O_2 + M \to HO_2 + M , \tag{5}$$

$$HO_2 + (H,OH,O) \to O_2 + (H_2,H_2O,OH) . \tag{6,7,8}$$
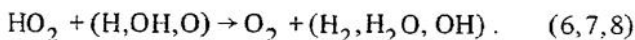
We have now measured radical recombination rates in fuel-lean $H_2/O_2/N_2$ flames at temperatures up to $2130°K$. The technique used was similar to that employed previously [2], i.e., hydrogen atom concentrations were measured in the burnt gas region of a set of isothermal flames having constant water vapour concentrations but various proportions of oxygen to nitrogen. The decay of hydrogen atoms has been shown to be accelerated considerably by increasing oxygen concentrations in the burnt gas.

Premixed hydrogen/oxygen/nitrogen flames were burnt on a flat-flame burner of similar design to that described by Padley and Sugden [8] except that an additional outer shield of hydrogen was used to reduce the effects of air entrainment.

A family of isothermal oxygen-rich flames with constant water concentration, but varying oxygen concentration, in the burnt gas was studied. The relative proportions by volume of the unburnt gas are shown in table 1. A hydrogen-rich flame at $2370°K$ was used to give an absolute calibration for hydrogen atoms [9].

Table 1

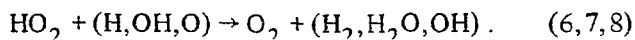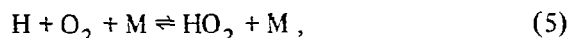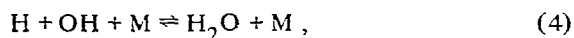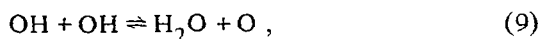| Flame no.	Volume proportion			Mean temperature ($^\circ$K)
	H_2	O_2	N_2	
1	2	1.2	4.8	
2	2	1.3	4.7	2130
3	2	1.4	4.6	
4	2	1.5	4.5	

Flame temperatures were measured by sodium D-line reversal and found to be the same within the experimental limits of the technique.

Hydrogen atom concentrations were determined by the lithium/lithium hydroxide method as modified by Halstead and Jenkins [2]. The use of this method in oxygen-rich flames has been discussed by McEwan and Phillips [10] and, for flames of similar temperatures and composition to those used here, the validity of the method has been confirmed.

Hydrogen atom concentrations were measured as a function of distance (and hence time, for this burner) from downstream of the reaction zone into the burnt gas. The short length of these oxygen-rich flames and the low hydrogen atom concentrations limit this distance to about 10 mm ($\equiv$ 1.06 msec) from the reaction zone.

2. Kinetic analysis and results

In the burnt gas region of fuel-lean $H_2/O_2/N_2$ flames the following reactions are considered to be important.

$$H + O_2 \rightleftharpoons OH + O ,\qquad (1)$$

$$OH + OH \rightleftharpoons H_2O + O ,\qquad (9)$$

$$H + OH + M \rightleftharpoons H_2O + M ,\qquad (4)$$

$$H + O_2 + M \rightleftharpoons HO_2 + M ,\qquad (5)$$

$$HO_2 + (H, OH, O) \rightarrow O_2 + (H_2, H_2O, OH) .\qquad (6,7,8)$$

For reaction (4) the relative third-body efficiencies of various species, M, have been determined [11] and show that (a) the efficiencies of O_2 and N_2 are similar and (b) for these flames the contribution of M =

H_2O is dominant. Loss of HO_2 via reactions (6), (7), and (8) must now be considered: (a) measurements of hydrogen atom concentrations in the burnt gas and subsequent calculations of hydroxyl radical and oxygen atom concentrations from the equilibria (1) and (9) show that [OH] $\geqslant$ 10[H] and 10[O]; (b) values of k_6, k_7 and k_8 are only approximately known [13], but from all available evidence it appears that $k_6 \approx k_7 \approx \frac{1}{2}k_8$. (However since reactions (6) and (7) account for the loss of two radicals and reaction (8) for only one, the *effective* rate constants are approximately equal.) Thus, it is concluded in the present work that to a good approximation reaction (7) accounts for the loss of HO_2.

Free radical concentrations in the burnt gas are related via balanced reactions such as (1) and (9) giving a state of partial equilibrium so that decay of radical concentrations towards full equilibrium must involve the total 'pool' of radicals. For this system

$$-d[R]/dt = 2k_7[HO_2][OH] + 2k_4[H][OH][M] ,\qquad (10)$$

where [R] is the total radical concentration = [H] + [OH] + 2[O] for these flames.

Assumption of a steady-state concentration for HO_2 gives

$$[HO_2] = k_5[H][O_2][M]/\{k_{-5}[M] + k_7[OH]\} .$$

When values are taken for k_{-5} from ref. [11], k_7 as 6×10^{12} cm^3 mole^{-1} sec^{-1} (ref. [13]) and values of [OH] calculated from the measured [H] values, it is readily shown that, at 2130°K, k_{-5}M $\gg k_7$[OH] so that $[HO_2] = K_5[H][O_2]$, where K_5 is the equilibrium constant for reaction (5).

By substituting for [OH] and [O] in terms of [H] in expression (10) [using equilibria (1) and (9), together with the steady-state concentration of HO_2], eq. (10) may be integrated to give

$$\frac{3}{[H]^{1/3}} + \frac{\alpha^{1/3}[O_2]^{1/3}}{3[H]} + \frac{2\beta^{1/3}[O_2]^{2/3}}{[H]^{2/3}}$$
$$= \{2k_7K_5[O_2] + 2k_4[M]\}\, \alpha^{1/3}[O_2]^{1/3}t ,\qquad (11)$$

where $\alpha = (K_1/K_9)[H_2O]$ and $\beta = K_1^2/K_9[H_2O]$.

Graphs of the left-hand side of expression (11) — called $f[H]$ — against time should thus be straight lines. A graph of the slopes of these lines divided by $\alpha^{1/3}[O_2]^{1/3}$ plotted against $[O_2]$ should also be a

straight line of slope = $2k_7 K_5$ and intercept = $2k_4[M]$. The results are shown in figs. 1 and 2 for flames at $2130°K$. Values of $k_7 = 1.2 \times 10^{13}$ cm^3 mole^{-1} sec^{-1} and $k_4[M] = 4.4 \times 10^{10}$ cm^3 mole^{-1} sec^{-1} may be derived from fig. 2, when K_5 is taken = 2.51×10^{-1} atm^{-1} (ref. [11]).

3. Discussion

It is apparent from previous work (e.g., ref. [2]) that the efficiencies of N_2 and O_2 as third bodies for reaction (4) are very similar and therefore that the observed increase in recombination rate indicated by the increasing slopes in fig. 1 with increasing $[O_2]$

cannot be attributed to an acceleration of reaction (4). Since the only change in concentration of bulk species in the burnt gas of these flames is a substitution of O_2 for N_2, the faster recombination rate must involve O_2, the most probable explanation of this being the participation of HO_2.

The reaction $H + O_2 + M \rightarrow HO_2 + M$ accounts for the second explosion limit in static, low-temperature systems and has been invoked to explain both the rate of heat release in flames at atmospheric pressure [5,6] and the rate of radical recombination in lean-shock-heated H_2/O_2 mixtures [7]. In many systems a major difficulty of analysis is caused by uncertainties regarding the fate of HO_2. In the flames used in this work, however, the problem is considerably sim-
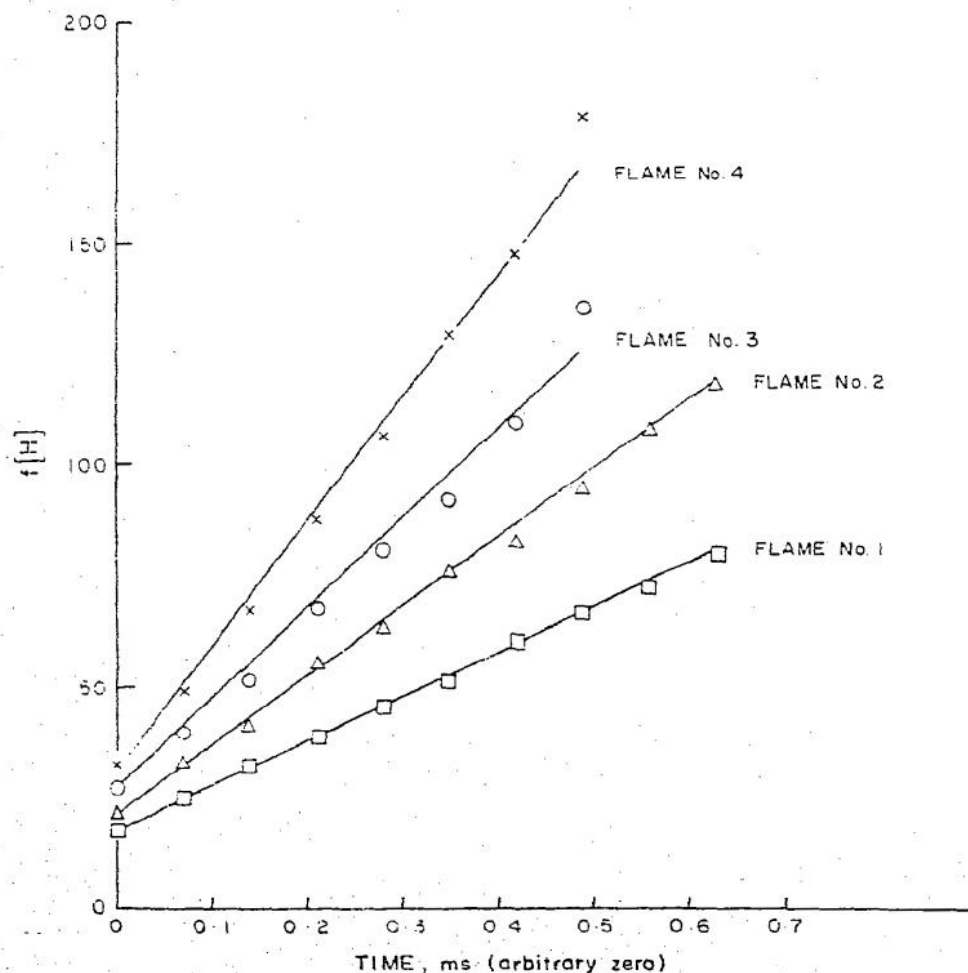

Fig. 1. Radical decay (as $f[H]$) in fuel-lean $H_2/O_2/N_2$ flames at $2130°K$.
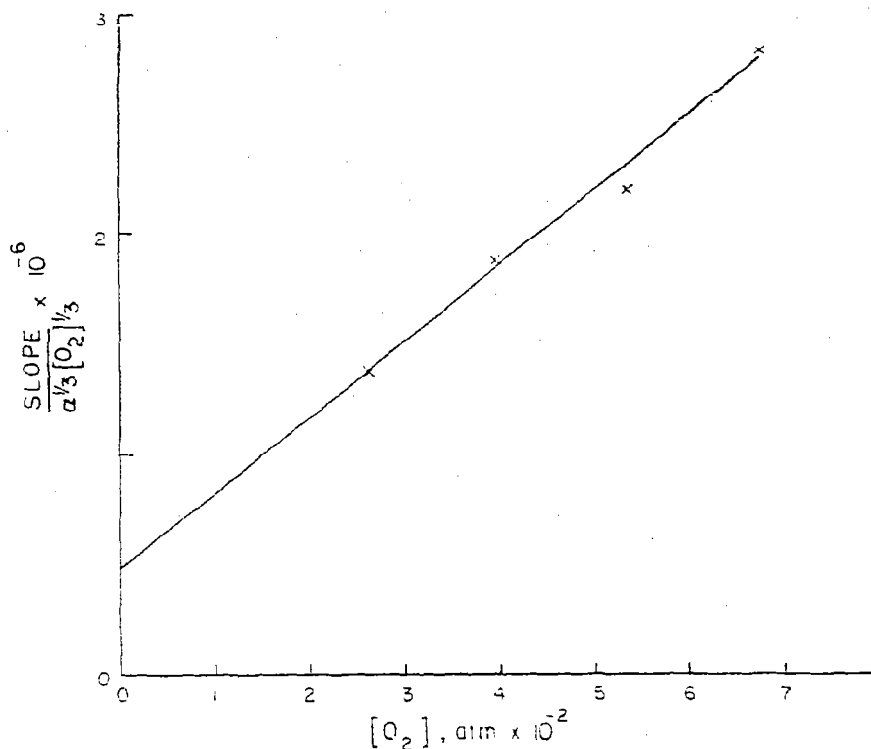
Fig. 2. (Slopes of lines in fig. 1)/$\alpha^{1/3}[O_2]^{1/3}$ against $[O_2]$.

plified by the predominance of OH as the main radical species and, as discussed earlier, it seems clear that the principal loss reaction is $HO_2 + OH \xrightarrow{7} H_2O + O_2$.

The rate constant for reaction (7) derived from the present results is 1.2×10^{13} cm^3 mole^{-1} sec^{-1} at 2130°K. A value for k_7 of between 10^{12} and 10^{13} cm^3 mole^{-1} sec^{-1} at 1000°K has been estimated recently by Troe [12] from work on the decomposition of H_2O_2. Schofield [13] has given a value of 6×10^{12} cm^3 mole^{-1} sec^{-1} at 273°K so that the value obtained in the present work substantiates these estimates. (The activation energy of reaction (7) is expected to be small.) The value found for $k_4[M]$ (4.4×10^{10} cm^3 mole^{-1} sec^{-1}) is in excellent agreement with a value of 4.3×10^{10} derived from previous flame work [2] and shock-tube work [3].

The assumptions made in deriving expression (11) seem justified for these flames at 2130°K — in particular the equilibration of reaction (5). At lower temperatures the rate of loss of HO_2 by reaction (5) becomes similar to loss by reaction (7), and the integrated rate expression becomes very complex. Neverthe-

less, similar experiments to those described here but with flames of lower temperatures confirm a considerable 'catalysis' of the radical recombination rate by O_2.

Principally, the results presented here demonstrate the importance of radical recombination via HO_2 even at flame temperatures up to 2130°K and the considerable acceleration — approximately threefold — of the overall recombination rate over that of the normal three-body process.

Acknowledgements

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