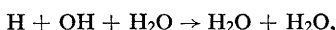


# THE RECOMBINATION OF HYDROGEN ATOMS AND HYDROXYL RADICALS IN HYDROGEN FLAME GASES

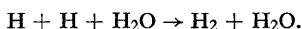
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The recombination of the free radicals H and OH in the burnt gases of hydrogen + oxygen + nitrogen burner flames at atmospheric pressure has been examined by flame photometric methods for temperatures in the range 1600–2400°K. The most important processes involved are considered to be

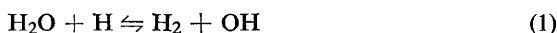


and



Values of velocity constants are deduced, and at 1650°K are  $1.5 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$  for the former reaction and  $6 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$  for the latter. They decrease slowly with increasing temperature.

Various methods involving flame photometry of traces of added substances have been developed in this laboratory for the measurement of the concentrations of the free radicals, atomic hydrogen and hydroxyl, in the burnt gases of premixed burner flames.<sup>1-4</sup> It has been shown that these free radicals are the most important minor constituents in the burnt gases from fuel-rich mixtures of hydrogen, oxygen and nitrogen, and that their concentrations are related to each other because of the balancing of the rapid reactions



Thus, since  $\text{H}_2\text{O}$  and  $\text{H}_2$  molecules are bulk constituents of the burnt gas, the ratio of concentrations  $[\text{H}]/[\text{OH}]$  is the same as the ratio of concentrations corresponding to full equilibrium  $[\text{H}]_e/[\text{OH}]_e$ , although the absolute levels of these concentrations may be different from the equilibrium ones. In general, it seems that radical concentrations much greater than equilibrium are generated by the main flame reactions at the narrow primary reaction zone near the burner. This effect is very marked for cooler flames (final temperature less than 2000°K). The concentrations of free radicals have been observed to decrease with increasing height in the flame gases in conformity with second-order kinetics in the radicals.<sup>1</sup> This is what would be expected from the recombination reactions

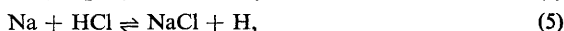


where X is a third body, in this case most probably a molecule of any of the bulk constituents  $\text{H}_2$ ,  $\text{H}_2\text{O}$  and  $\text{N}_2$ . It is the purpose of this paper to report some detailed measurements on these recombinations and to attempt to elucidate some of the associated ternary velocity constants.

## EXPERIMENTAL

The experimental method for the production of shielded flames of premixed hydrogen, oxygen and nitrogen has already been described in detail, as well as the methods of measuring flame temperatures (Na D-line reversal) and the techniques of flame photometry of traces of various additives.<sup>5</sup> As previously, all the experimental flames were on the fuel-rich side, which gave good cylindrical columns of burnt gas. The concentrations

of atomic hydrogen were measured in three ways. Two of these are absolute methods, depending on the knowledge of the equilibrium constants for the balanced reactions,



respectively, and measurements of the concentrations of all species except atomic hydrogen. The third one <sup>2</sup> is relative and is based on measurements of the intensity of the head of the 0, 0 band of CuH at 4280 Å. CuH appears to be formed in the flame gases by the balanced reaction



the balance lying well to the left, and to have thermal electronic excitation. Thus, apart from a thermal factor for the variation of intensity with temperature and a number of minor corrections,<sup>2</sup> the band intensity may be taken as a relative measure of [H]. This last method is the simplest in operation and it has been used in this work to measure the relative values of [H] for a series of flames with temperatures in the range of 1600-2400°K, at various heights above the burner. Conversion to absolute values has been made by the use of the first method mentioned above for one selected flame.

The decrease of radical concentrations with increasing height is converted into a function of time by calculating the vertical flow rate of the burnt gas from the rate of supply of the unburnt gas, the cross-section of the column of burnt gas, the room temperature, and the final flame temperature. These flow rates were of the order of 10<sup>3</sup> cm/sec.

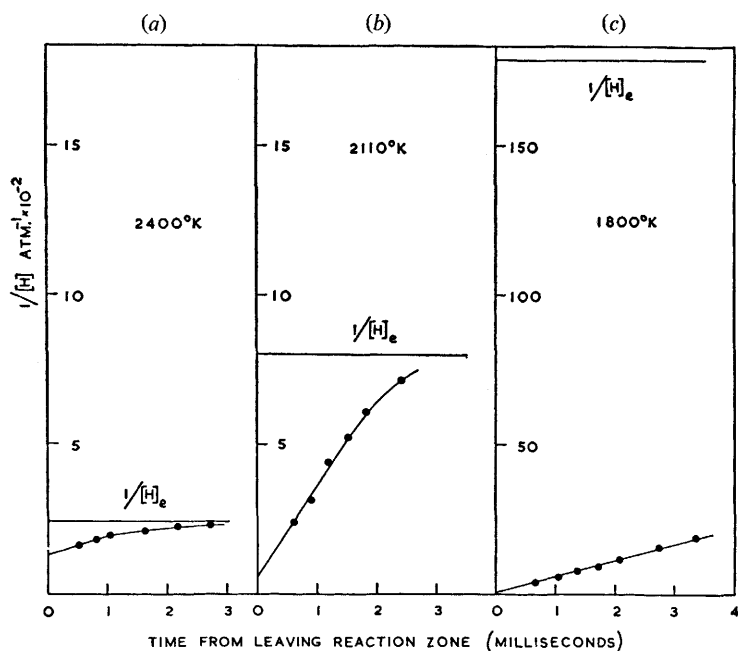


FIG. 1.—H atom recombination.

## RESULTS

Typical results for the variation of  $1/[\text{H}]$  with time from leaving the reaction zone are shown in fig. 1 (a, b, c) for three flames. Good straight lines are obtained at the two lower temperatures, and a marked curve at the highest. If radical recombination is taking place through reactions (2) and (3), reaction (1) being balanced, then such straight lines will be expected, since the corresponding kinetic law is

$$1/[\text{H}] - 1/[\text{H}]_0 = k't, \quad (7)$$

where  $[\text{H}]_0$  is the initial (reaction zone) value of [H], provided  $[\text{H}] \gg [\text{H}]_e$ . The level of  $[\text{H}]_e$  is indicated in the diagram and it will be seen that the required inequality holds

well for the coolest flame, and over a fair range for the intermediate one. In the hottest flame,  $[H]$  is never very different from its equilibrium value.

The fact that  $[OH]$  changes linearly with  $[H]$  (as a consequence of the balance of reaction (1)) up to about 2.5 msec from leaving the burner is shown by fig. 2. At times greater than this the shielding of the inner flame becomes less effective and the influence of further burning of the excess hydrogen with entrained air, with consequent rapid increase in hydroxyl concentration, becomes apparent.

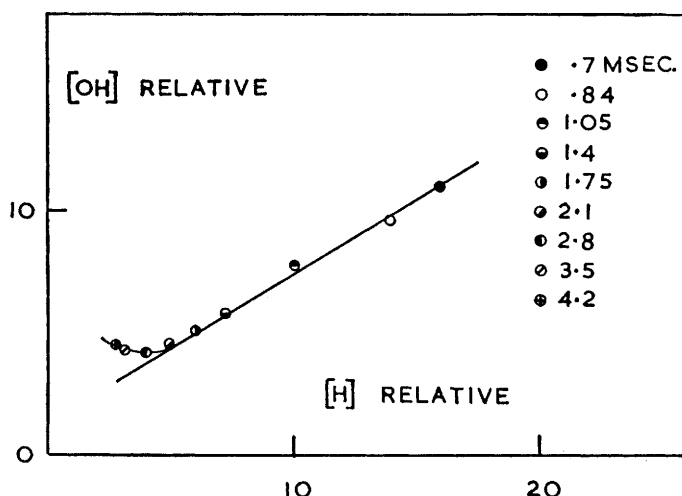


FIG. 2.—Relation between  $[H]$  and  $[OH]$  in a typical flame.

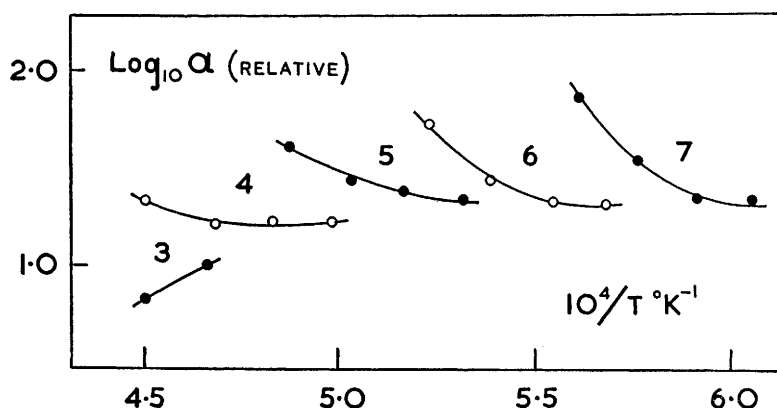


FIG. 3.—Radical recombination in flames of different composition and at different temperatures.

Relative  $[OH]$  has been converted to absolute  $[OH]$  using the absolute values of  $[H]$  and the equilibrium constant  $K_1$  of the reaction  $H_2O + H \rightleftharpoons H_2 + OH$  computed from the data of Gaydon and Wolfhard.<sup>6</sup>

If the reactions (2) and (3) are the only ones to make a significant contribution to the decay of free radicals, then the apparent second-order velocity constant  $k'$  of eqn. (7) may be written as

$$k' = (k_2 + k_3 K_1 [H_2O]/[H_2]) / (1 + K_1 [H_2O]/[H_2]), \quad (8)$$

where  $k_2$  and  $k_3$  are apparent second-order velocity constants for reactions (2) and (3). The numerator of this expression, denoted by  $a$  has been calculated, and plotted logarithmically against  $1/T$  in fig. 3. The points for the four highest temperatures are dubious, because of the lack of linearity in the corresponding diagrams of the type of fig. 1, from which the values of  $k'$  have been deduced.

$k_2$  and  $k_3$  are, of course, composite, since they will depend on the concentrations of all the three major constituents, which can act as third bodies. Each group, or "family" of points in fig. 3 corresponds to flames with a fixed  $[N_2]/[O_2]$  ratio in the unburnt gases, shown in the diagram as a number against each family. Higher temperatures in a given family correspond to compositions nearer to stoichiometry. The unburnt  $[H_2]/[O_2]$  ratio ranged from 4.0 to 2.5 within each family.

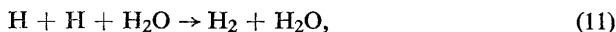
## DISCUSSION

The full problem is the elucidation of the six ternary velocity constants given by

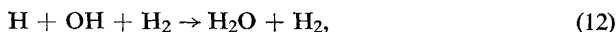
$$k_2 = k_{2(H_2O)}[H_2O] + k_{2(H_2)}[H_2] + k_{2(N_2)}[N_2], \quad (9)$$

$$k_3 = k_{3(H_2O)}[H_2O] + k_{3(H_2)}[H_2] + k_{3(N_2)}[N_2], \quad (10)$$

each of which will, in general, be a function of temperature. It might be supposed that the six values corresponding with a particular temperature could be resolved from experiments on six isothermal flames, but this is not the case. For example, the reactions,



and



are physically indistinguishable in this system because of the operation of the balanced reaction (1). In addition, unfortunately,  $[H_2O]$  is almost constant in a series of isothermal flames, which limits the number of significantly different independent relations which can be derived, as  $([H_2] + [N_2])$  is then necessarily also almost constant. A more restricted approach must therefore be adopted.

It is not unreasonable to assume that  $H_2O$  will have the highest efficiency as a third body for both recombination reactions, as it is triatomic and therefore has a greater number of degrees of freedom available for the redistribution of the energy liberated by the recombination. It was found by Russel and Simons<sup>7</sup> that for the recombination of iodine atoms, the relative efficiency of different additives depends on the intermolecular force fields, as reflected in boiling points and critical temperatures. The efficiencies of  $H_2O$ ,  $H_2$  and  $N_2$  were found to be approximately in the ratio 10 : 1 : 1. The fact that  $H_2O$  has the highest efficiency or that the relative efficiencies of  $N_2$  and  $H_2$  as third bodies are approximately the same in the flame gases may be demonstrated in the following way. Either of these conditions would make  $k_2$  and  $k_3$  independent of composition at any one temperature; then a plot of  $a$  against  $K_1[H_2O]/[H_2]$  for a series of isothermal, hydrogen-rich flames should be a straight line with intercept  $k_2$  on the ordinate axis and slope  $k_3$ . Such a plot is shown in fig. 4, for seven flames at 1890°K. It is a good straight line.

If  $H_2O$  is by far the most important third body, it is then reasonable to suppose that  $k_2 = k_{2(H_2O)}[H_2O]$  and  $k_3 = k_{3(H_2O)}[H_2O]$ , and to calculate the ratio  $k_3/k_2$ , which will be independent of the bulk flame gas composition, and will be a function of temperature only. Over the whole temperature range, in which  $[N_2]$  varies by 4-fold and  $[H_2]$  by 6-fold, this ratio takes the value of  $24 \pm 5$ . This supports the view that  $H_2O$  is practically the only efficient third body. The frequency factor for collisions of H and OH will be expected to be greater than that for collisions of H with H, both on account of the higher collision diameter of OH and because of the greater possibility of "sticky collisions", so that the value of the ratio  $k_3/k_2$  which has been deduced seems not unreasonable.

In fig. 5,  $\log_{10} k_{3(H_2O)}[H_2O]$  is plotted against  $1/T$ , giving a smooth curve of low slope. The large curvature towards high temperatures is probably erroneous, since in these flames  $[H]$  is near  $[H]_e$ , making the deduction of velocity constants inaccurate.

The low positive slope at lower temperatures indicates that radical recombination is more rapid at these temperatures ( $[H_2O]$  varies only very slowly). A similar result was obtained by Russel and Simons<sup>7</sup> for the recombination of iodine atoms in the presence of rare gases and of certain hydrocarbons, and more recently by several groups of workers,<sup>8-11</sup> for the recombination of bromine

atoms in the presence of argon. Strong, Chien, Graf and Willard<sup>8</sup> consider that this effect may be due to the fact that the duration of the "sticky collisions" which must be the first stage in the recombination probably decreases with increasing temperature.

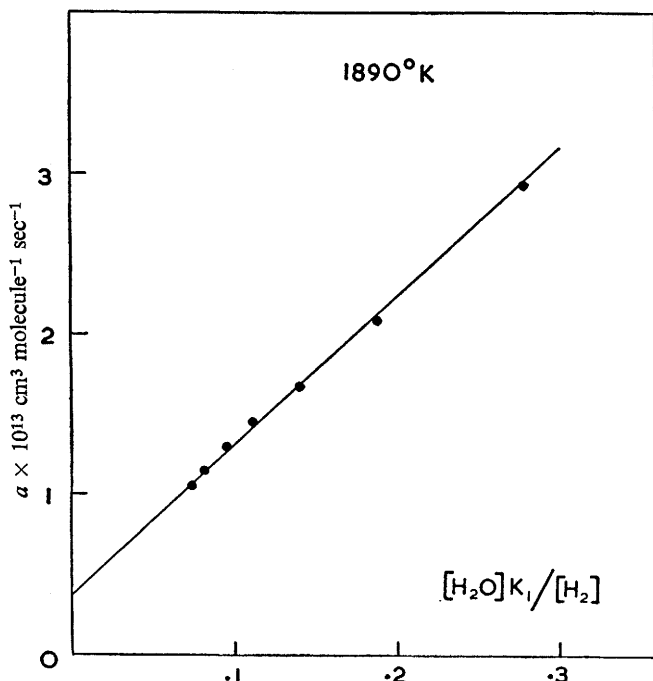


FIG. 4.—Radical recombination in isothermal flames.

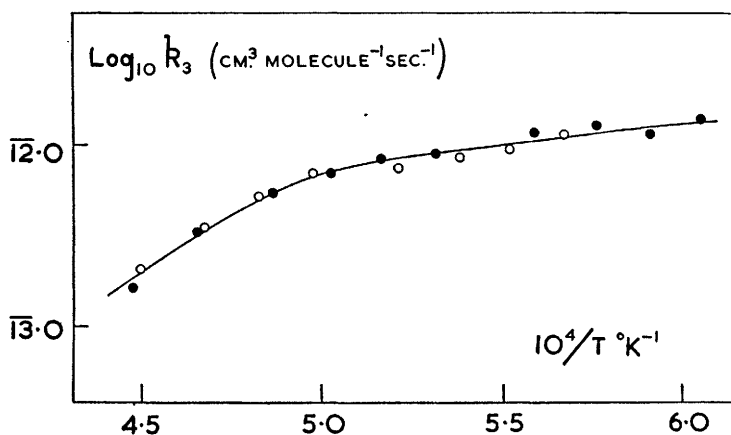


FIG. 5.— $k_3$  as a function of temperature.

Recently an overall rate constant for radical recombination has been measured in similar flames by Padley and Sugden,<sup>12</sup> using a completely independent method (based on the energy release caused by the recombination of excess free radical concentrations in the neighbourhood of the reaction zone). Their results agree well with  $k_3(\text{H}_2\text{O})$  of the present work, as is shown in table 1, and therefore support the conclusion reached here. Previous work on these reactions is rather scattered.

The rate of disappearance of OH radicals produced by an electrical discharge through water vapour was investigated by Oldenberg and Rieke.<sup>13</sup> They stated that they were unable to distinguish between the reactions  $\text{H} + \text{OH} + \text{X} \rightarrow \text{H}_2\text{O} + \text{X}$  and  $\text{OH} + \text{OH} + \text{X} \rightarrow \text{H}_2\text{O}_2 + \text{X}$ , followed by very rapid decay of the  $\text{H}_2\text{O}_2$  formed, but considered the first reaction to be much more probable.

TABLE 1

flame temp. °K	velocity constants ( $\text{cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ )	
	$k_3(\text{H}_2\text{O})$ (this work)	overall rate constant for radical recombination with $\text{H}_2\text{O}$ as third body (Padley and Sugden <sup>12</sup> )
2270	$1.5 \times 10^{-31}$	$2.7 \times 10^{-31}$
2290	1.8	1.7
2195	3.4	3.7
2165	3.3	4.6
2110	5.1	5.7
2085	5.3	2.1

In any case  $\text{H}_2\text{O}_2$  is too unstable to merit consideration in our systems. They obtained for the rate constant  $k_3(\text{H}_2\text{O})$  a value of  $1.35 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$  at  $300^\circ\text{C}$ . The present work gives for  $k_3(\text{H}_2\text{O})$ ,  $1.5 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$  at  $1650^\circ\text{K}$ , the lowest temperature at which measurements were made. It is difficult to compare results of determinations made at widely different temperatures and under different conditions, but if the rate of radical recombination changes slowly with temperature the agreement can be considered to be fairly satisfactory.

No data seem to be available for the rate of recombination of H atoms in the presence of water vapour, but a number of determinations of the rate constant have been made under conditions when  $\text{H}_2$  molecules acted as third bodies.<sup>14, 15, 16</sup> The values given do not seem to be very reliable, as they vary over a factor of about 10, but are of the order of  $1 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ , at or near to  $300^\circ\text{K}$ . If the ratio  $k_3/k_2$  is about 24, the present work leads to  $k_2(\text{H}_2\text{O}) = 6 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ , at  $1650^\circ\text{K}$ . This figure is higher than the approximate figure quoted above, but two factors have to be borne in mind; the efficiency of  $\text{H}_2\text{O}$  as a third body for the recombination of H atoms is probably higher than that of  $\text{H}_2$ , and radical recombination is more rapid at lower temperatures. Thus any comparison of the results with other work is difficult. The results are of value, however, in that they establish beyond reasonable doubt the nature of the recombination reactions in flame gases, and give some information about their relative rates.

One of us (E. M. B.) is grateful to Girton College for their award of a Research Fellowship.

<sup>1</sup> Bulewicz, James and Sugden, *Proc. Roy. Soc. A*, 1956, **235**, 89.

<sup>2</sup> Bulewicz and Sugden, *Trans. Faraday Soc.*, 1956, **52**, 1475.

<sup>3</sup> Bulewicz and Sugden, *Trans. Faraday Soc.*, 1956, **52**, 1481.

<sup>4</sup> James and Sugden, *Proc. Roy. Soc. A*, 1958, in press.

<sup>5</sup> James and Sugden, *Proc. Roy. Soc. A*, 1955, **227**, 312.

<sup>6</sup> Gaydon and Wolfhard, *Flames* (Chapman and Hall, London, 1953).

<sup>7</sup> Russel and Simons, *Proc. Roy. Soc. A*, 1953, **217**, 271.

<sup>8</sup> Strong, Chien, Graf and Willard, *J. Chem. Physics*, 1957, **26**, 1287.

<sup>9</sup> Britton and Davidson, *Abstr. Minneapolis Meeting Amer. Chem. Soc.*, p. 40R, Sept. 1955.

<sup>10</sup> Britton, Davidson and Schott, *Faraday Soc. Discussions*, 1954, **17**, 58.

<sup>11</sup> Palmer and Hornig, *J. Chem. Physics*, 1957, **26**, 98.

<sup>12</sup> Padley and Sugden, 1958, in press.

<sup>13</sup> Oldenberg and Rieke, *J. Chem. Physics*, 1939, **7**, 485.

<sup>14</sup> Steiner, *Trans. Faraday Soc.*, 1935, **31**, 623.

<sup>15</sup> Farkas and Sachsse, *Z. physik. Chem. B*, 1934, **27**, 111.

<sup>16</sup> Smallwood, *J. Amer. Chem. Soc.*, 1934, **56**, 1542.