

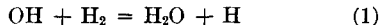
# THE KINETICS OF HYDROGEN-ATOM RECOMBINATION

F. S. LARKIN AND B. A. THRUSH

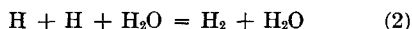
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The homogeneous recombination of hydrogen atoms has been studied in a fast flow system at temperatures between 200° and 350°K, using a calorimetric probe technic. Data for argon as third body agree with shock-tube studies of the dissociation reaction in the presence of argon, the over-all temperature dependence of the recombination reaction being close to  $T^{-1}$ . Experiments in which water was added to the discharge products show that water is not particularly effective as a third body in contrast to its behavior in the  $H + O_2$  combination.

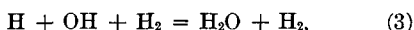
Direct studies<sup>1-3</sup> of the kinetics of atom and radical recombination in flame gases are frequently difficult to interpret in terms of individual rate constants. In addition to the presence of many species which may have different third-body efficiencies, the rapidity with which certain equilibria are established makes it impossible to isolate particular recombination processes. For example, the rapidity with which the equilibrium



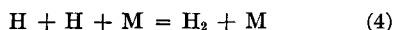
is established in the outer cone of a hydrogen-air flame makes it impossible to distinguish between the recombination reactions<sup>1</sup>



and



both of which might be expected to be more rapid than the recombination reaction



for  $M = H_2, N_2$ .

In the last few years, several studies of the dissociation of hydrogen in shock tubes<sup>4-7</sup> have yielded rate constants for Reaction (4) at temperatures between 2500° and 4000°K, particularly for  $M = H_2$  and Ar. On the other hand, data on hydrogen-atom recombination around room temperature, where the rate constants for more complex third bodies could be determined, are limited to determinations made before 1940<sup>8-10</sup> when the conflicting desiderata for obtaining accurate rate constants from discharge-flow experiments were not fully understood.

This paper reports current studies of hydrogen-atom recombination in a discharge-flow system at and around ambient temperatures. For the

determination of reliable rate constants for this reaction, the hydrogen-atom concentration must be measured accurately at many points along the flow tube. An isothermal calorimeter probe<sup>11,12</sup> was selected for this purpose since it is an absolute measuring device of high sensitivity and can be moved along the flow tube readily. Its accuracy is dependent, however, both on complete recombination occurring on the probe and on the probe detecting all the heat released on recombination. Any variation of probe efficiency with hydrogen-atom concentration or with gas composition or pressure would seriously affect the measurements, and a double-probe system was therefore used, in which a second isothermal calorimeter, placed approximately 3 cm downstream from the first probe, monitored its performance. The efficiency of such a system has been verified by the HNO emission technic.<sup>13,14</sup> This latter technic was not used for kinetic studies in this system, since it has to be calibrated by an independent method before it can give absolute concentrations.

In the design of a flow system for the study of hydrogen-atom recombination, care must be taken to avoid errors due to gradients of pressure, composition, and temperature. Kaufman<sup>15</sup> has discussed the solution of these problems in the study of oxygen-atom reactions, and his criteria are readily adapted to the study of hydrogen atoms.

## Experimental

Hydrogen atoms were produced by passing pure hydrogen, or hydrogen in an inert gas carrier (containing less than 10% hydrogen), through a 100-W, 17-mcps rf discharge. The discharge was established in an 8-mm-i.d. quartz tube between two external aluminium-foil electrodes with forced-air cooling. The discharge

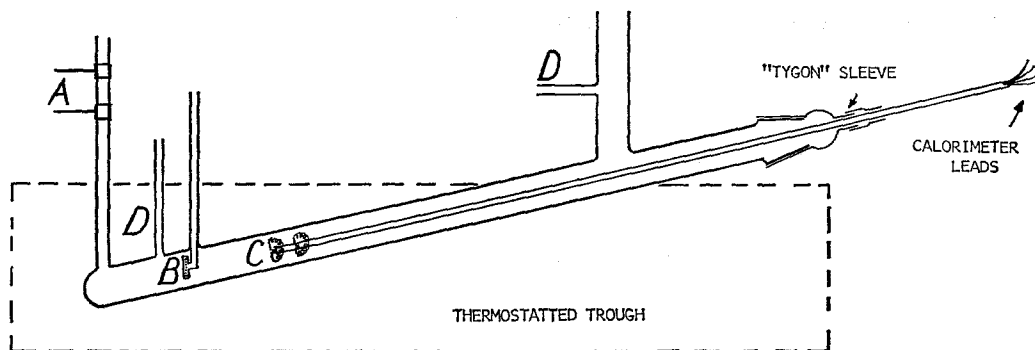


FIG. 1. Schematic diagram of flow line. A, electrodeless discharge; B, mixing jet; C, isothermal calorimeters; D, leads to manometers.

products flowed into a Pyrex glass reaction tube, 2.5 cm i.d. and 100 cm long, at the upstream end of which was a multiple inlet jet for the introduction of reactants with rapid mixing (Fig. 1). The flow tube was inclined so that it could be immersed in a well-lagged copper trough. This contained water for experiments at or above ambient temperature; acetone was used below room temperature. The internal surfaces of the discharge and reaction tubes were coated with a thin layer of "Dri-film" to reduce surface recombination.

Hydrogen-atom concentrations were measured by means of a sliding isothermal calorimeter which was inserted into the reaction tube through the downstream end. A "Tygon" sleeve provided the vacuum seal for the glass tube carrying the leads to the head of the calorimeter. Two calorimeters were used, each consisting of 50 cm of 34 S.W.G. 13% rhodium-platinum wire wound into a spiral. Each spiral was connected to a separate Wheatstone bridge and they were mounted in tandem about 3 cm apart so that the downstream calorimeter could be used to determine the recombination efficiency of the first spiral, which was always greater than 80%.

Experiments were conducted at total pressures between 1 and 7 mm Hg, with flow velocities between 250 and 1000 cm/sec. Pressures at each end of the reaction tube were measured with silicon oil manometers. Hydrogen-atom concentrations of up to 5% were obtained.

Cylinder argon, "mineral" helium, and "high purity" hydrogen were obtained from the British Oxygen company. Recombination rate constants were found to depend strongly on the drying and purification of these gases, which is described in the next section.

## Results

Preliminary experiments showed that the concentration of hydrogen atoms produced in the

discharge depended greatly on the presence of trace impurities in the hydrogen used. In particular, small amounts of water catalyze the production of hydrogen atoms, a phenomenon which has been noted and used by previous workers,<sup>8,9</sup> perhaps sometimes unconsciously in the case of syrupy phosphoric-acid coatings for discharge tubes.<sup>10</sup> The presence of water reduces the rate of surface recombination for hydrogen atoms and appears to render the surface more uniform in this respect. The rate of homogeneous recombination of hydrogen atoms is increased,

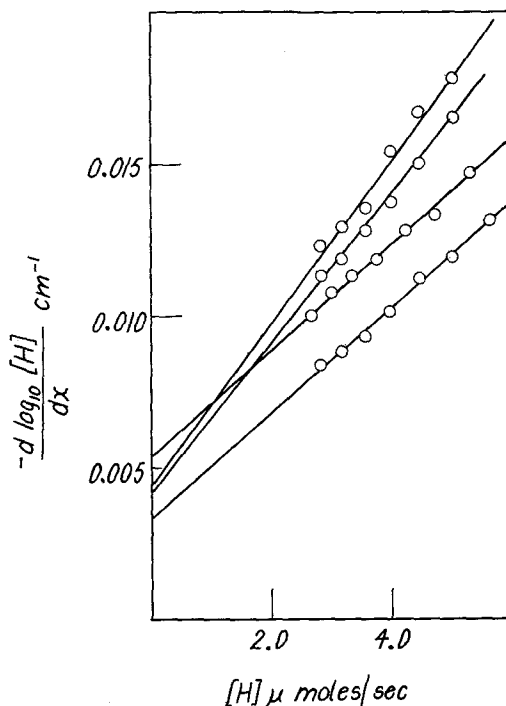
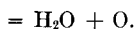
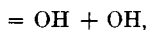
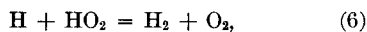
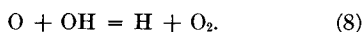
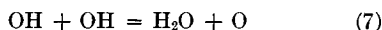


FIG. 2. Typical plots of  $-d \log_{10} [H]/dt$  against  $[H]$  for the homogeneous recombination of hydrogen atoms in an argon carrier.

however, when moisture is present in the hydrogen which is passed through the discharge. This acceleration appears to be first order in atomic hydrogen and is almost certainly due to the reactions<sup>16</sup>



In addition to reactions in the discharge which might convert water to molecular oxygen, OH radicals formed in the discharge yield oxygen by the rapid reactions<sup>17</sup>



Since these observations, the hydrogen used has been purified by passing it through a "Deoxo" unit followed by a trap at  $-196^\circ\text{C}$  and atmospheric pressure containing finely divided silica gel supported on glass wool. Argon was also purified by passage at atmospheric pressure through a  $\text{P}_2\text{O}_5$  trap and a trap containing finely divided silica gel supported on glass wool and cooled to  $-80^\circ\text{C}$ . Under these conditions, sufficient dissociation (1% to 5% hydrogen atoms) could only be obtained if not less than 10% argon was added to the hydrogen passing through the discharge.

Values of the third order rate constant  $k_4$  for hydrogen-atom recombination defined by the equation

$$-d[\text{H}]/dt = \sum_{\text{M}} k_{4,\text{M}}[\text{H}]^2[\text{M}] + k_s[\text{H}],$$

where  $k_s$  refers to the heterogeneous recombination, were determined by plotting  $d \ln [\text{H}]/dt$  against  $[\text{H}]$ . Typical data are shown in Fig. 2. The rate constants determined to date are given in Table I.

Addition of up to 10% water vapor to hydrogen atoms in an argon carrier downstream from the discharge did not produce a detectable increase

TABLE I

M	$T$ ( $^\circ\text{K}$ )	$10^{-15} k_4$ ( $\text{cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$ )
$\text{H}_2$	293	$6.8 \pm 1$
Ar	213	$5.6 \pm 0.5$
Ar	293	$4.5 \pm 0.5$
Ar	349	$4.0 \pm 0.5$
$\text{H}_2\text{O}$	293	$>50$

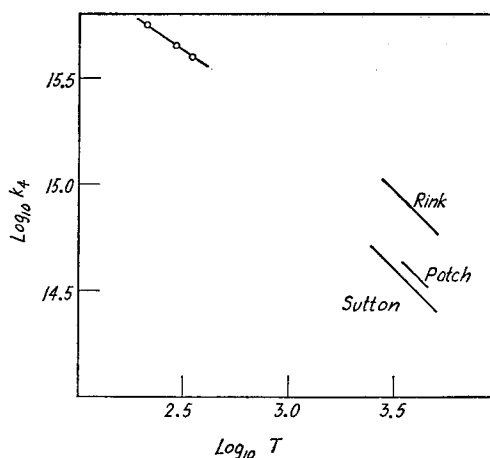


FIG. 3. Plot of  $\log_{10} k_4$  against  $\log_{10} T$ , comparing the present data with shock-tube data on the dissociation by argon.

in the rate of homogeneous recombination of hydrogen atoms. It did, however, decrease the rate of surface recombination on the first spiral of the calorimeter. These observations were confirmed by measurements of  $\text{HNO}$  emission. It was concluded that for  $\text{M} = \text{H}_2\text{O}$ ,  $k_4$  is not greater than  $5 \times 10^{16} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$  at  $293^\circ\text{K}$ .

## Discussion

The value reported here for  $\text{M} = \text{H}_2$  is slightly lower than that given by a recent reanalysis of older data<sup>18</sup> on similar studies at room temperature. This difference could arise from the presence of water in the hydrogen used in the earlier work.

Figure 3 is a log-log plot in which the temperature dependence of the data for  $\text{M} = \text{Ar}$  is compared with shock-tube studies in which the dissociation of hydrogen was followed by electronic absorption spectroscopy (Patch<sup>6</sup>), x-ray densitometry (Rink<sup>6</sup>), and interferometry (Sutton<sup>7</sup>). The general agreement is good, although the over-all temperature dependence of  $k_4$  seems to be closer to the  $T^{-1}$  form used by these workers in the interpretation of their shock-tube data than the  $T^{-1/2}$  dependence observed in our experiments. It should be noted that only in Sutton's experiments was a  $T^{-1}$  dependence of  $k_4$  observed, it merely was assumed by the other workers. The heterogeneous recombination of hydrogen atoms on glass surfaces was found to have a positive temperature coefficient which could easily affect the value found for the negative temperature coefficient of the homogeneous reaction in discharge-flow experiments.

The relative efficiencies of argon, hydrogen, and water as third bodies in Reaction (4) are 1:1.5:>10 at room temperature; these may be compared with the corresponding ratios for other third-order combination reactions involving hydrogen atoms. For Reaction (5), the corresponding ratio is 1:5:30 at 800°K, determined from the second explosion limit of the hydrogen-oxygen reaction.<sup>19,20</sup> The ratio of the values of  $k_3$  for argon



and hydrogen as third-bodies<sup>14</sup> is 1:1.7 at room temperature. This is closer to the ratio for Reaction (4) than for Reaction (5), a surprising observation in view of the similarity in structure and bond-dissociation energy which exists between HNO and HO<sub>2</sub>. Recent studies<sup>21</sup> of the efficiencies of a wide range of third bodies in the  $\text{H} + \text{O}_2$  and  $\text{D} + \text{O}_2$  reactions show a very complex pattern of behavior. This cannot be attributed to the higher temperature used in their work, as the only extensive data on the temperature coefficients of a recombination reaction (iodine atoms) for a wide range of third bodies<sup>22,23</sup> show that the rate constants for different third bodies become more similar as the temperature is raised.

For this reason, and because we have not found a particularly high efficiency for water as third body in the recombination of hydrogen atoms, it seems most appropriate to compare our data with flame studies assuming that all the abundant species in hydrogen-air flames give similar values of  $k_4$ . Making this assumption, Kaskan<sup>2</sup> obtained a value of  $k_4 = 4 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$  at 1500°K. Applying this assumption to the data of Bulewicz and Sugden and of Dixon-Lewis, Sutton, and Williams,<sup>3</sup> give values of  $k_4 = 6 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$  at 1650°K and  $5 \times 10^{15} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$  at 1273°K, respectively. It can be seen that the agreement between the different workers is good, and that their values are generally consistent with the shock-tube data and those obtained at room temperature. This supports the view that acceleration of hydrogen-atom decay observed in flames with increasing ratios of  $[\text{H}_2\text{O}]/[\text{H}_2]$  must be attributed to Reaction (3) rather than to Reaction (2).

#### ACKNOWLEDGMENT

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#### COMMENTS

*Dr. M. A. Khan (Shell Research Ltd., Thornton):* Is it possible to give some quantitative idea of the corrections for radical diffusion, axial diffusion, pressure drop, and wall effect?

*Dr. B. A. Thrush:* Normally we analyze our data by plotting  $d \log[\text{H}]/dt$  against  $[\text{H}]$ . The slope of

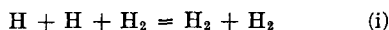
this gives the rate constant of the homogeneous reaction, and the intercept the rate of the surface reaction. The latter is small enough that the correction for radial diffusion is wholly negligible.

Under normal conditions, the correction for back diffusion is about 0.5%, and it never exceeds 2.0% under any conditions. The pressure drop was meas-

ured directly; again the normal correction was about 0.5% and the maximum less than 2.0%.

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*Dr. G. Dixon-Lewis (University of Leeds):* The value reported in this paper for Reaction (i)

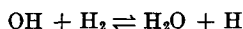


of  $k_1 = 0.68 \pm 0.1 \cdot 10^{16} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$  at 293°K, is somewhat lower than that suggested by other estimates of this reaction. These values can be correlated, within a factor of 2, by the expression  $k_1 = 10^{18.85} T^{-1}$ , although it is not impossible that some curvature occurs in the lower temperature region (<1000°K). This might be caused by an intermediate complex  $\text{H}_3$ . The mean value given by this expression at 293°K, is  $2.4 \times 10^{16} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$ , compared with  $0.68 \times 10^{16} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$  given in this paper.

*Dr. B. A. Thrush:* We consider that most of the previous values, determined at room temperature, are too high, due to the presence of moisture in the hydrogen used. This applies to all the pre-1940 experiments reviewed by Wise and Ablow and by Careri. More experiments clearly are needed, both at low and intermediate temperatures.

♣

*Dr. G. L. Schott (Los Alamos Scientific Laboratory):* From spectrophotometric measurements of the rate of disappearance of OH radicals during the recombination phase of the hydrogen-oxygen reaction behind shock waves in mixtures of 1%  $\text{O}_2$ , 4% and 8%  $\text{H}_2$ , and 95% and 91% Ar, Bird and I [Schott, G. L. and Bird, P. F.: "Kinetic Studies of Hydroxyl Radicals in Shock Waves. IV. Recombination Rates in Rich Hydrogen-Oxygen Mixtures", J. Chem. Phys., to be published] have deduced a value of the rate coefficient for recombination of two hydrogen atoms in the presence of Ar atom as third body. Maintenance of equilibrium in the reversible reaction



during recombination in these rich mixtures, was assumed in interpreting the results. These measurements were made between 1400° and 2000°K and yielded  $\log_{10} k_4 = 14.9 \pm 0.2$  in this temperature range. Inclusion of such a point in Fig. 3 of the paper of Larkin and Thrush, supports their conclusion that  $k_4$  is approximately inversely proportional to the first power of temperature between room temperature and the regime of dissociation rate measurements.

*Mr. C. G. Dunkle (APL/The Johns Hopkins University):* It looks as if the data of Rink, Patch,

and Sutton in Fig. 3 all indicate a  $T^{-1}$  dependence of  $k_4$ , whereas the slope of the line of Thrush's data indicates, rather than a  $T^{-1/2}$  dependence, something more like  $T^{-0.6}$ .

*Dr. B. A. Thrush:* The agreement with Schott's data is very satisfying. The temperature coefficient of our data, near room temperature, corresponds to  $T^{-0.6 \pm 0.2}$ . In the shock-tube work, only Sutton reports a  $T^{-1}$  dependence; both Patch and Rink assumed this form.

More data are needed, particularly at low and intermediate temperatures, before the form of the  $\log k/\log T$  plot can be uniquely determined. Unfortunately, the range of measurements in discharge-flow systems is limited by increased surface recombination, both at high and low temperatures.

♣

*Dr. K. L. Wray (Avco Everett Research Laboratory):* With respect to the high relative catalytic efficiencies of H and  $\text{H}_2\text{O}$  to Ar in the reaction



(measured at 800°K) as compared with those for the reactions



and



measured at room temperature, the authors point out that (from studies of I-atom recombination) the efficiency of different third bodies become more similar as the temperature is raised. This is not the case for O-atom recombination, and probably not the case for N-atom recombination. The catalytic efficiency of  $\text{O}_2$  (relative to Ar) must certainly exhibit a maximum as the temperature is increased. In the absence of a theoretical model, it is not clear if such behavior is to be found for the above reactions, and if so, at what temperature the maximum occurs.

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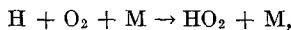
*Prof. B. de B. Darwent (Catholic University of America):* The relative efficiencies of Ar,  $\text{H}_2$ , and  $\text{H}_2\text{O}$  in deactivating  $\text{HXY}$ , quoted in the paper, are quite different. Is this difference real or due only to the fact that the HNO reaction was investigated directly, whereas the  $\text{HO}_2$  reaction data were obtained from the explosion limit work?

Measurements of the relative efficiencies of He,  $\text{N}_2$ ,  $\text{CO}_2$ ,  $\text{CF}_4$ , and  $\text{SF}_6$  in deactivating NOCl are in good agreement with the data for HNO. All the polyatomics are of approximately equal efficiency. Similar work with  $\text{HO}_2^*$  has shown that  $\text{CO}_2$ ,  $\text{CF}_4$ , and  $\text{SF}_6$  are also of equal efficiency.

*Dr. M. A. Khan (Shell Research Ltd., Thornton):* Is the difference in the efficiency of  $\text{H}_2\text{O}$  as a third body (M) in the reactions



and



due to the nature of the collision complex, or is there some other reason?

*Dr. B. A. Thrush:* It is unfortunate that iodine-atom recombination is the only reaction for which the efficiencies of a wide range of third bodies have been measured as a function of temperature. For the reactions discussed here ( $\text{H} + \text{H}$ ,  $\text{H} + \text{O}_2$ , etc.), the

very limited data suggest that the relative efficiencies of different third bodies do not vary greatly with temperature; for instance, we have found the relative efficiencies of argon and water, in the reaction  $\text{H} + \text{O}_2$  at 300°K, to be similar to those at 800°K.

For reactions yielding triatomic molecules, the behavior should be tending towards that observed in the pyrolysis of organic molecules, where most large molecules give very similar efficiencies and the values for the inert gases are up to a factor of ten lower. The data so far available support this view. However, the work of Linnett and Selley on the  $\text{H} + \text{O}_2$  and  $\text{D} + \text{O}_2$  recombination reactions, shows that specific vibrational transfer must be invoked in addition to the general effects of collision number and molecular complexity, in order to explain the relative efficiencies they obtained.