

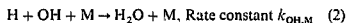
# Rates of $\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$ and $\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$ Reactions in Flames

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Measurements of radical recombination rates in hydrogen-oxygen flames previously reported have been reanalyzed to give improved values for the rate constants of  $\text{H} + \text{H} + \text{M} \rightarrow \text{H}_2 + \text{M}$  and  $\text{H} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O} + \text{M}$  reactions. The new analysis takes into account the rates of the reverse reactions and utilizes an improved technique for obtaining individual rate constants from the overall rates. The revised values (in units of  $10^{13} \text{ ml}^2 \text{ mole}^{-2} \text{ sec}^{-1}$ ) at  $\sim 1900^\circ \text{K}$  are as follows:  $k_{\text{H},\text{Ar}} = 1.8$ ;  $k_{\text{OH},\text{Ar}} = 3.2$ ;  $k_{\text{H},\text{He}} = 1.8$ ;  $k_{\text{OH},\text{He}} = 8.0$ ;  $k_{\text{H},\text{N}_2} = 1.9$ ;  $k_{\text{OH},\text{N}_2} = 3.2$ ;  $k_{\text{OH},\text{H}_2\text{O}} = 27$ ;  $k_{\text{H},\text{CO, CO}_2} = 5.4$ ;  $k_{\text{OH},\text{CO, CO}_2} < 3.6$ ;  $k_{\text{H},\text{H}_2\text{O}} + Kk_{\text{OH},\text{H}_2} = 3.6$ .

In a previous publication [1] we reported measurements of the overall radical recombination rates in hydrogen-oxygen flames. These rates were analyzed to give values for the rate constants of reactions 1 and 2:



with argon, helium, nitrogen, water, carbon monoxide, or carbon dioxide as the third body, M.

Since this publication, we have reanalyzed our measurements, (a) allowing for the rates of the reverse dissociative reactions, and (b) using an analytical method which utilizes linear functions to obtain the values of the  $k_{\text{H},\text{M}}$  and  $k_{\text{OH},\text{M}}$  rather than the quadratic functions used previously. As a result of this reanalysis we have obtained more accurate values for the

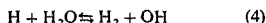
radical recombination rate constants, and we report these new values here.

The experimental measurements were of hydrogen atom concentration,  $[\text{H}]$ , as a function of time,  $t$ , from the reaction zone. In place of the plots of  $1/[\text{H}]$  against  $t$  previously used to obtain the overall recombination rate,  $k_o$ , plots of  $\log ([\text{H}] + [\text{H}]_e)/([\text{H}] - [\text{H}]_e)$  against  $t$  have been used here, where  $[\text{H}]_e$  is the equilibrium value of  $[\text{H}]$ . This form of the second-order plot, which takes the reverse dissociative reaction into account [2], has a slope of  $2k_o/[\text{H}]_e$ .

Values of  $k_o$  obtained from the slopes of these logarithmic plots for the flames containing steam as diluent were resolved into the component rate constants  $k_{\text{OH},\text{H}_2\text{O}}$  and  $(k_{\text{H},\text{H}_2\text{O}} + Kk_{\text{OH},\text{H}_2})$  by carrying out a least-squares fit to the expression

$$\frac{k_o([\text{H}_2] + K[\text{H}_2\text{O}]) - 2k_{\text{H},\text{H}_2}[\text{H}_2]^2}{[\text{H}_2\text{O}]^2} = 2(k_{\text{H},\text{H}_2\text{O}} + Kk_{\text{OH},\text{H}_2}) \frac{[\text{H}_2]}{[\text{H}_2\text{O}]} + 2Kk_{\text{OH},\text{H}_2\text{O}} \quad (3)$$

which follows readily from the analysis given in Ref. 1.  $K$  is the equilibrium constant for reaction 4:



The values of  $k_{\text{H},\text{H}_2}$  used to evaluate the left-hand side of Eq. 3 were those employed previously [3]. No significant temperature dependence of the rate constants having been

found over the temperature range  $\sim 1800$ – $2000^\circ\text{K}$ , the results were analyzed together at a mean temperature of  $\sim 1900^\circ\text{K}$ . From the slope and intercept of this plot the values of  $(k_{\text{H},\text{H}_2\text{O}} + Kk_{\text{OH},\text{H}_2})$  and  $k_{\text{OH},\text{H}_2\text{O}}$  shown in Table 1 were obtained.

The flames with argon, helium, and nitrogen as diluents were analyzed by carrying out a least-squares fit to the expression

$$\frac{1}{[M]} \left\{ \frac{k_6([H_2] + K[H_2O])}{2} - (k_{\text{H},\text{H}_2}[H_2]^2 + \{k_{\text{H},\text{H}_2\text{O}} + Kk_{\text{OH},\text{H}_2}\}[H_2][H_2O] + K[H_2O]^2 k_{\text{OH},\text{H}_2\text{O}}) \right\} = k_{\text{H},\text{M}}[H_2] + K[H_2O] k_{\text{OH},\text{M}} \quad (5)$$

where  $[M]$  is the diluent concentration, and the values of  $(k_{\text{H},\text{H}_2\text{O}} + Kk_{\text{OH},\text{H}_2})$  and  $k_{\text{OH},\text{H}_2\text{O}}$  used were those determined from the analysis of the steam flames using expression 3. The groups of flames at different nominal temperatures of  $1800^\circ\text{K}$  and  $2000^\circ\text{K}$  were treated as one set at  $\sim 1900^\circ\text{K}$  in the same manner as the steam flames. One typical plot is shown in Fig. 1, and results obtained from the slopes and intercepts of the plots (together with the essentially constant value for  $[H_2O]$ ) are given in Table 1.

As discussed in Ref. 1, rate data from flames containing carbon dioxide as diluent can, in theory, be analyzed to give values of some of the individual rate constants for  $M = \text{CO}$  and  $\text{CO}_2$ . In practice, however, the data are not sufficiently accurate to make the separation practicable. The data from these flames have

therefore been analyzed by means of Eq. 5, with the assumption that carbon monoxide and carbon dioxide have equal third-body efficiencies. The results are shown in Table 1. As the data of this work did not enable a satisfactory determination of  $k_{\text{OH},\text{M}}$  ( $M = \text{CO}, \text{CO}_2$ ) to be made, the value for this rate constant shown in Table 1 is an upper limit only.

The reanalysis of the results for the steam flames has led to a larger value of  $k_{\text{OH},\text{H}_2\text{O}}$  and a smaller value for the inseparable sum  $(k_{\text{H},\text{H}_2\text{O}} + Kk_{\text{OH},\text{H}_2})$  than those reported formerly. The sub-

Table 1. Values of Rate Constants Obtained (ca.  $1900^\circ\text{K}$ )

Diluent, M	Rate Constant, $\text{ml}^2 \text{mole}^{-2} \text{sec}^{-1}$	
	$10^{-15} k_{\text{H},\text{M}}$	$10^{-15} k_{\text{OH},\text{M}}$
Argon, Ar	$1.8 (\pm 0.7)$	$3.2 (\pm 1.5)$
Helium, He	$1.8 (\pm 0.7)$	$8.0 (\pm 2.0)$
Nitrogen, $\text{N}_2$	$1.9 (\pm 0.7)$	$3.2 (\pm 2.5)$
Water, $\text{H}_2\text{O}$	...	$27 (\pm 3.0)$
Carbon oxides ( $\text{CO}, \text{CO}_2$ )	$5.4 (\pm 1.0)$	$< 3.6$

$$(k_{\text{H},\text{H}_2\text{O}} + Kk_{\text{OH},\text{H}_2}) = 3.6 \pm 0.4 \times 10^{15} \text{ ml}^2 \text{mole}^{-2} \text{sec}^{-1}$$

$$K = 0.0845 \text{ at } 1900^\circ\text{K}$$

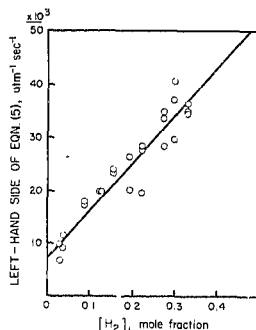


Figure 1. Plot of left-hand side of Eq. 5 against  $[H_2]$  for hydrogen-oxygen-helium flames at  $2000^\circ\text{K}$ .

sequent use of these new values in the analysis of the flames with the other diluents has led to smaller values of  $k_{H,N_2}$ ,  $k_{H,He}$ ,  $k_{OH,Ar}$ , and  $k_{OH,N_2}$ .

Most previous determinations of  $k_{OH}$  by shock-tube and flame studies have been for  $M = H_2O$  and  $Ar$  [4-13]. Our new results for these two third bodies are in good agreement with much of this work, as may be seen from the detailed comparison recently shown in Ref. 6. The only significant departures from the expression for  $k_{OH,H_2O}$  given by Homer and Hurlle [6] are the high results of Refs. 8, 11, and 13. In these cases, however,  $H_2O$  was assumed to be the only third body of importance, and these values are, therefore, upper limits for  $k_{OH,H_2O}$ .

Our new value for  $k_{OH,N_2}$  of  $3.2 \times 10^{15} \text{ ml}^2 \text{ mole}^{-2} \text{ sec}^{-1}$ , compared with  $4.7 \times 10^{15}$  obtained originally, is still considerably lower than the three values reported previously [4, 5, 8], even when allowance is made for the differences in temperature. No explanation of this difference can be given at present.

The recalculated values for  $k_{H,N_2}$  and  $k_{H,Ar}$  are lower than our original ones. However, they remain appreciably larger than the results reported from other flame [4, 5] and shock-tube studies [7], with the exception of the  $k_{H,Ar}$  value obtained by Hurlle et al. [3], from whose results we calculate  $k_{H,Ar} = 1.8 \times 10^{15}$  at  $1915^\circ K$ . The disagreement of flame results and shock-tube results between themselves and each other suggests that a factor-of-2 accuracy is about the best that can be achieved with present techniques for recombination rate constants.

There appears to be little difference between third-body efficiencies for hydrogen atom recombination. This finding is in agreement with the observations of Getzinger and Blair [7],

Azatyan et al. [14], and Bennett and Blackmore [15], who find third-body coefficients, relative to  $H_2$ , of  $Ar = 1.3-1.7$ ,  $He = 1.1-1.3$ , and  $N_2 = 1.1$ , respectively, at room temperature.

*It is a pleasure to acknowledge the assistance of members of the Mathematics Research and Services Division of Thornton Research Centre with the computations.*

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(Received November, 1969;  
revised February, 1970)