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Citation: *J. Chem. Phys.* **41**, 2869 (1964); doi: 10.1063/1.1726368

View online: <http://dx.doi.org/10.1063/1.1726368>

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# Kinetic Studies of Hydroxyl Radicals in Shock Waves. IV.\* Recombination Rates in Rich Hydrogen-Oxygen Mixtures

GARRY L. SCHOTT AND PAUL F. BIRD

*University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico*

(Received 18 June 1964)

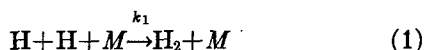
The rate of disappearance of OH following  $[\text{OH}]_{\text{max}}$  in shocked  $\text{H}_2\text{-O}_2\text{-Ar}$  mixtures has been measured by a refined ultraviolet line absorption technique. Thirty-one experiments have been done with mixtures of 4%  $\text{H}_2$ , 1%  $\text{O}_2$ , 95% Ar; 2%  $\text{H}_2$ , 0.5%  $\text{O}_2$ , 97.5% Ar; and 8%  $\text{H}_2$ , 1%  $\text{O}_2$ , 91% Ar at initial pressures between 50 and 200 mm Hg. The approximate rate equation found to describe the OH disappearance is  $-d[\text{OH}]/dt = k_{\text{apparent}}[\text{OH}]^2[M]$ , where  $[M]$  is total gas concentration. Assuming that the equilibrium relationship  $\alpha = [\text{OH}]/[\text{H}] = K[\text{H}_2\text{O}]/[\text{H}_2]$  is maintained, and that the recombination reactions are:



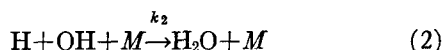
$k_{\text{apparent}}$  may be interpreted as  $(A/\alpha)(k_1 + \alpha k_2)$  where  $A$  is a factor near unity which incorporates the definitions of the  $k$ 's as volumetric rate coefficients, the small variation of  $\alpha$  and density during the reaction, and the participation of O and  $\text{O}_2$ .  $(k_1 + \alpha k_2)$  increased linearly with  $\alpha$  between  $\alpha = 0.01$  and  $\alpha = 0.1$ , yielding  $k_1 = 6 \pm 1 \times 10^8 \text{ liter}^2 \text{ mole}^{-2} \text{ sec}^{-1}$  and  $k_2/k_1 \approx 10 \pm 5$ . No dependence on temperature was evident. Estimation of the contributions of  $\text{H}_2$ , H, and  $\text{H}_2\text{O}$  as third bodies indicates that  $k_1^{\text{Ar}} = 4 \pm 2 \times 10^8 \text{ liter}^2 \text{ mole}^{-2} \text{ sec}^{-1}$  near 1700°K.

## INTRODUCTION

PREVIOUS work<sup>1,2</sup> in rich hydrogen-oxygen-diluent flames has shown that, in the final stage of the combustion reaction, several reversible reaction steps are maintained substantially in equilibrium, while net progress is achieved by the removal of excess species through three-body recombination reactions. The reversible reactions couple the recombination paths, so that each recombination reaction has the same departure from equilibrium, expressed as the ratio of equilibrium constant to the quotient of the activities of products and reactants, and a single measurement serves to determine the chemical composition. Kinetics studies in such flames<sup>3,4</sup> have shown that the important recombination reactions are



and



and have provided values of the rate coefficients  $k_1$  and  $k_2$  under flame conditions.

Observations on this reaction system in shocked gas mixtures have been reported in earlier papers of the present series<sup>5-7</sup> and have indicated establishment of equilibrium conditions in the reversible reaction steps promptly at the end of the induction period. This paper reports measurements of the kinetics of the slow disappearance of OH following its maximum concentration in shocked  $\text{H}_2\text{-O}_2\text{-Ar}$  mixtures.

## EXPERIMENTAL METHODS

Basic shock-wave techniques and the ultraviolet line absorption method of determining OH concentration have been discussed in Part I.<sup>5</sup> However, many modifications of apparatus and procedures have been incorporated in the present work, and it is appropriate to present the methods used in this investigation.

The dimensions of the circular shock tube were: internal diameter, 10 cm throughout; driver-chamber length, 192 cm; test-chamber length, 373 cm. Its construction was of brass, and the interior surface of the test chamber was plated with nickel to decrease its porosity. Single- and multiple-layer brass shim stock diaphragms were used. Evacuation of the test chamber was accomplished through a side port located 13 cm from the diaphragm position. Final evacuation was done with an NRC B-2 oil diffusion-ejection booster pump backed by a Kinney KC 5 mechanical pump. Vacuum measurements in the test chamber were made

\* Work performed under the auspices of the U.S. Atomic Energy Commission. This paper, in an earlier form, was preprinted by and presented before the Division of Fuel Chemistry, American Chemical Society, 147th National Meeting, Philadelphia, Pennsylvania April 1964.

<sup>1</sup> E. M. Bulewicz, C. G. James, and T. M. Sugden, *Proc. Roy. Soc. (London)* **A235**, 89 (1956).

<sup>2</sup> W. E. Kaskan, *Combust. Flame* **2**, 229 (1958).

<sup>3</sup> G. Dixon-Lewis, M. M. Sutton, and A. Williams, *Discussions Faraday Soc.* **33**, 205 (1962).

<sup>4</sup> J. L. J. Rosenfeld and T. M. Sugden, *Combust. Flame* **8**, 44 (1964).

<sup>5</sup> S. H. Bauer, G. L. Schott, and R. E. Duff, *J. Chem. Phys.* **28**, 1089 (1958).

<sup>6</sup> G. L. Schott and J. L. Kinsey, *J. Chem. Phys.* **29**, 1177 (1958).

<sup>7</sup> G. L. Schott, *J. Chem. Phys.* **32**, 710 (1960).

with a CVC Philips gauge connected to a side port midway along its length.

Shock velocity measurement was made by a series of five deposited platinum resistor gauges. These gauges were 1 mm by 6 mm and had resistances between 30 and 200  $\Omega$ . They were flush mounted with the shorter dimension disposed axially at intervals of 60.00, 50.00, 30.00, and 29.94 cm, beginning 198 cm from the diaphragm. The gauge outputs were amplified, shaped by 2D21 thyatrons, echoed after 6.25  $\mu$ sec, mixed with 10- $\mu$ sec timing marks, and presented on an oscilloscope raster<sup>8</sup> operating at 100  $\mu$ sec/line. A modified Tektronix 545 instrument was used.

The quartz windows for the light beam used in measuring OH concentrations were located 1.3 cm downstream from the fourth velocity gauge, some 34 cm from the end of the shock tube. This setup allowed several hundred microseconds for observation of the moving gas behind the incident shock wave before the arrival of the reflected wave from the end plate or the hydrogen driver gas from upstream.

The optical train from the flash discharge lamp to the photomultiplier detector was mounted independently of the shock tube. The flash lamp was operated in the way described in Part I.<sup>6</sup> The lamp itself differed, however, in that the H<sub>2</sub>O vapor pressure was regulated at 0.9 mm Hg by NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>·3H<sub>2</sub>O+NaC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> at 0°C. At this working pressure the luminosity was much freer of spurious fluctuations in intensity than at higher pressures, and its intensity was only slightly diminished. A 2.5-cm-focal-length spherical lens immediately in front of the lamp focused the luminous region inside the toroidal anode crudely at the monochromator entrance slit 70 cm away, providing condensation of the beam in the (vertical) direction along the 2-mm-by-10-mm collimating slits on either side of the shock-tube windows. The luminous region itself was substantially as wide as the slits. At the monochromator entrance slit a crude  $f=1.0$  cm cylindrical lens was used with its axis parallel to the slit to condense the beam onto the entrance slit and provide for filling the width of the grating. The 1P28 photomultiplier detector was placed immediately outside the exit slit of the monochromator.

The anode resistor used was 22 k $\Omega$ , and 4 ft of RG-71 cable delivered the signal to the input terminal of a Type L preamplifier in a Tektronix Type 545 oscilloscope. Thus the electronic response time was about 2  $\mu$ sec, which approximately matches the time inhomogeneity in the gas sample within the 2-mm width of the beam. Faster response can be achieved, but for recombination rate measurements over periods like 10<sup>-4</sup> sec it is unnecessary, and reduction in statistical noise is achieved by relaxing the time resolution.

The oscilloscope photographs contained, in addition to the light transmission record, a base line of zero

photoelectric signal, and in displaced positions, a trace bearing timing marks and a trace of the unabsorbed photoelectric signal from a separate flashing of the lamp. This monitor trace was synchronized with the lamp firing in the same way as in the experimental trace. It was needed because the lamp signal, while reproducible in shape, was not quite constant over the time of the experiment.

The JACO model 8200 monochromator was operated in an air thermostat at 36°±1°C. The first-order spectrum was used with the entrance slitwidth 0.050 mm and the exit slitwidth 0.570 mm. The instrument was calibrated with a low pressure mercury discharge spectrum and set to transmit air wavelengths uniformly between 3088.7 and 3097.3 Å, with transmission decreasing linearly to zero at wavelengths less than 3087.9 Å or greater than 3098.1 Å. Precision of the calibration and thermal stability are estimated as ±0.3 Å. Photographic spectra made with film held against the exit slit confirmed the isolation of the lines<sup>9</sup> between  $R_{20}(\lambda_{\text{air}}=3089.0 \text{ Å})$  and  $Q_8(\lambda_{\text{air}}=3096.8 \text{ Å})$ .

Experimental gas mixtures were prepared manometrically from commercial cylinder gases in a thoroughly evacuated glass-lined (domestic hot water) tank and heated from beneath to be mixed by diffusion and convection for at least 24 h before use. Mass-spectrographic analysis of each batch confirmed the absence of unintended components beyond traces of N<sub>2</sub> and CO<sub>2</sub>.

Experiments without the flash lamp energized have shown that with this experimental arrangement, the intensity of light emitted by the reacting gases was at least three orders of magnitude less than that which reached the detector when the lamp was flashed. Thus the OH concentration was determined strictly by absorption spectrophotometry.

## DATA REDUCTION

The raw data obtained in each experiment consist of the recorded initial conditions, the shock velocity data contained in the photograph from the raster oscilloscope, and the OH concentration data contained in the oscilloscope photograph of the photoelectric signal. Prior to any chemical kinetics analysis these data are reduced to the apparent OH concentration as a function of time under particular conditions of temperature, pressure, and concentrations of other species. These preliminary data reduction procedures are discussed first.

## Shock Velocity

Evaluation of the shock-wave velocity from the gauge positions and shock arrival times was done by adjusting each time for small differences in circuitry

<sup>8</sup> H. T. Knight and R. E. Duff, *Rev. Sci. Instr.* **26**, 257 (1955).

<sup>9</sup> G. H. Dieke and H. M. Crosswhite, *J. Quant. Spectry. Radiative Transfer* **2**, 97 (1962).

response (corrections of a few tenths of a microsecond), fitting the five  $x, t$  data points to the quadratic expression  $t = a + bx + cx^2$ , and evaluating  $(dt/dx)^{-1}$  at the observation window position. From least-squares treatment, the indicated uncertainty in  $b$ , which is most of the uncertainty in  $dt/dx$ , was usually a few tenths of a percent. In a few cases it was as great as 1%, indicating irregular behavior of the shocks and/or the detection system. The coefficient  $c$  was always small and usually positive, indicating that the shock velocity did undergo small changes as the shock progressed along the tube. In the subsequent analysis, however, no correction for this effect was made, and the velocity was treated as being a constant.

### Hugoniot Calculations

Solution of the Rankine-Hugoniot equations was carried out by means of a computer code<sup>10</sup> to obtain the temperature, density, and composition behind each shock wave as functions of the initial conditions, the shock velocity, and the progress of chemical reaction. The computations for equilibrium conditions were obtained straightforwardly by the general method of Brinkley<sup>11</sup> which is incorporated in the shock equations code. The restricted equilibrium computations for selected extents of recombination less than the final equilibrium extent were made by arbitrarily constraining<sup>12</sup> the number of moles per original mole of material in the system. The species Ar, H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, OH, H, and O were considered in the computations. Ideal gas thermodynamic functions for H<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>O, OH, and O were obtained from the JANAF tables<sup>13</sup> and formulated for interpolation in the polynomial form used previously in this laboratory.<sup>10,14</sup> The polynomial coefficients for Ar and H were evaluated directly from the formulas for monatomic gases with no internal excitation.

### Determination of [OH]

The calibration curve relating absorbance and OH concentration used in the earlier work was an empirical one based on observations of equilibrium gases in shock waves. For the present work, a much more refined method has been developed. It is a semiempirical method based in part on absorbance measurements in equilibrium shocked gas, but it makes use of the fundamental molecular properties of OH to extend the calibration to regimes of OH concentration, temperature, and pressure where equilibrium observations could not be made.

The calibration program consists of three parts: (1) experimental determination of the spectral intensity distribution of our OH line source, (2) formulation of the absorption spectrum of OH on the basis of theory using parameters which may be derived from independent experiments, and (3) numerical synthesis of the response of thermal absorber to the lamp spectrum in order to account for the experimentally determined absorbance of equilibrium mixtures. The details of these steps are being reported separately; the methods used and their application to the old, higher-pressure lamp spectrum are described elsewhere.<sup>15</sup>

The principal features of the calibration are summarized as follows. The line shapes and relative intensities in the lamp spectrum were determined from high dispersion photographic spectrograms made by repeated flashes. The source spectrum and the absorber spectrum were each described in the computations by superposition of lines having combined Doppler and Lorentz broadening.<sup>16</sup> The line strengths given by Dieke and Crosswhite<sup>9</sup> as modified by Learner<sup>17</sup> were used. The populations of the absorbing states were related to the total OH concentration assuming complete internal thermal equilibrium. The values of the transition probability coefficient  $F$  and the pressure-broadening parameter  $a$  (as defined in the literature<sup>18</sup>) used to describe the measured equilibrium absorbances were  $F = 3.50 \times 10^{-4}$  and  $a = 335P(\text{atm})/T(^{\circ}\text{K})$ . These values may be compared with values of  $F$  between  $1.23 \times 10^{-4}$  and  $2.68 \times 10^{-4}$  reported by other workers<sup>19</sup> and Kaskan's<sup>20</sup> estimate of  $a$ . Perhaps the present calibration is not significantly more accurate than the old empirical one in the regime where the latter was determined, but the extension to other regimes is superior, and the whole calibration is on a much firmer basis.

The absorbance ( $-\log_{10}$  of the fractional transmission) of the incident spectrum was computed for sets of values of the absorber temperature, pressure, and optical density (product of OH concentration and path length) covering the ranges of these parameters involved in the experiments. A numerical interpolation scheme was used to derive the OH concentrations for a series of absorbance values during each experiment. For this purpose an average temperature and pressure for each experiment were obtained as the means of the values computed for partial equilibrium conditions with zero recombination and complete equilibrium

<sup>10</sup> P. F. Bird, R. E. Duff, and G. L. Schott, Los Alamos Scientific Lab. Rept. LA 2980, 1964.

<sup>11</sup> S. R. Brinkley, Jr., *J. Chem. Phys.* **15**, 107 (1947).

<sup>12</sup> G. L. Schott, *J. Chem. Phys.* **40**, 2065 (1964).

<sup>13</sup> *JANAF Interim Thermochemical Tables* (The Dow Chemical Company, Midland, Michigan, 1960), and supplements through December 1962.

<sup>14</sup> R. E. Duff and S. H. Bauer, *J. Chem. Phys.* **36**, 1754 (1962).

<sup>15</sup> P. F. Bird, "Absorbance of the OH Radical in a Specific Wavelength Interval near 3090 Å," thesis, Department of Physics, University of New Mexico, 1961.

<sup>16</sup> S. S. Penner, *Quantitative Molecular Spectroscopy and Gas Emissivities* (Addison-Wesley Publishing Company, Reading, Massachusetts, 1959), Secs. 3-5 and 4-4.

<sup>17</sup> R. C. M. Learner, *Proc. Roy. Soc. (London)* **A269**, 311 (1962).

<sup>18</sup> T. Carrington, *J. Chem. Phys.* **31**, 1243 (1959).

<sup>19</sup> D. M. Golden, F. P. Del Greco, and F. Kaufman, *J. Chem. Phys.* **39**, 3034 (1963).

<sup>20</sup> W. E. Kaskan, *J. Chem. Phys.* **31**, 944 (1959).

conditions. The absorbance for each optical density in the table was first interpolated to the appropriate temperature and then the appropriate pressure. Finally the several measured absorbances were interpolated to optical densities and hence OH concentrations. A quadratic interpolation formula was used in each step, with two of the three values of the independent variable bracketing the desired value.

### Rate Equation

The rate equation for the disappearance of OH in a reacting mixture of  $H_2$ ,  $O_2$ ,  $H_2O$ , OH, H, and O is developed for conditions of variable-density shock-wave flow in a manner which incorporates the recombination mechanism, Reactions (1) and (2), and anticipates the insertion of partial equilibrium relationships among the several species. Let us define the mole number of each species  $n_i$  by the relationship

$$\rho n_i = [I], \quad (3)$$

where  $\rho$  is the density in grams per liter and  $[I]$  is the concentration of Species  $I$  in moles per liter. We then identify the partial derivative with respect to time  $(\partial[I]/\partial t)_p = \rho dn_i/dt$  as the net volumetric rate of chemical production of Species  $I$ .<sup>21</sup>

Now it has been shown that<sup>1,2,22</sup> in the system being considered, relating the total volumetric rate of production of all species to the combined chemical recombination rate from all paths  $R_{\text{recomb}}$  leads to

$$\rho d(n_H + n_{OH} + 2n_O + 2n_{O_2})/dt = -2R_{\text{recomb}}. \quad (4)$$

To formulate  $n_H$ ,  $n_O$ , and  $n_{O_2}$ , and their derivatives in terms of the measured  $[OH]$ , we proceed as follows. Let

$$[OH] = \alpha[H]. \quad (5)$$

Then

$$n_{OH} = \alpha n_H, \quad (6)$$

and

$$\frac{\rho dn_H}{dt} = \frac{\rho}{\alpha} \frac{dn_{OH}}{dt} - \frac{\rho n_{OH}}{\alpha^2} \frac{d\alpha}{dt}. \quad (7)$$

Similarly, let

$$[O] + [O_2] = \beta[OH]^2, \quad (8)$$

so that

$$n_O + n_{O_2} = \beta \rho n_{OH}^2, \quad (9)$$

and

$$\frac{\rho d(n_O + n_{O_2})}{dt} = \frac{2\beta \rho n_{OH}^2 dn_{OH}}{dt} + \frac{\rho^2 n_{OH}^2 d\beta}{dt} + \frac{\beta \rho n_{OH}^2 d\rho}{dt}. \quad (10)$$

The scale of time  $t$  experienced by an element of shocked gas is converted to the scale  $\tau$  at an observation point stationary with respect to the unshocked

gas by

$$dt = (\rho/\rho_0) d\tau, \quad (11)$$

where  $\rho_0$  is the density of the unshocked gas.

The variables  $\rho$ ,  $\alpha$ , and  $\beta$  are considered as functions of the variable  $[OH]$ . Then from the definition, Eq. (3), it follows that

$$\rho dn_{OH}/dt = d[OH]/d\tau (1 - d \ln \rho / d \ln [OH]). \quad (12)$$

Finally, for conditions in which the recombination mechanism consists of Reactions (1) and (2) and all dissociation rates are negligible, we express the total recombination rate  $R_{\text{recomb}}$  in terms of concentrations and conventional rate coefficients by

$$R_{\text{recomb}} = k_1[M_1][H]^2 + k_2[M_2][H][OH], \quad (13)$$

where  $[M_1]$  and  $[M_2]$  are the total gas concentrations acting as third bodies in recombination Reactions (1) and (2).

Then substitution of Eq. (5)–(13) into Eq. (4) and rearrangement of terms leads to

$$\begin{aligned} \frac{\alpha d(1/[OH])}{d\tau} = & 2 \left( \frac{\rho}{\rho_0} \right) (k_1[M_1] + \alpha k_2[M_2]) \\ & \times \left\{ (1 + \alpha + 4\alpha\beta[OH]) \left( 1 - \frac{d \ln \rho}{d \ln [OH]} \right) - \frac{d \ln \alpha}{d \ln [OH]} \right. \\ & \left. + 2\alpha\beta[OH] \left( \frac{d \ln \beta}{d \ln [OH]} + \frac{d \ln \rho}{d \ln [OH]} \right) \right\}^{-1}. \quad (14) \end{aligned}$$

For convenience we now refer to the factor 2 and the complicated expression in braces on the right-hand side of Eq. (14) as  $A$ , and for lack of more specific information, identify the third-body concentrations  $[M_1]$  and  $[M_2]$  with the total gas concentration  $[M]$ . Thus the rate coefficients are referred to the experimental gas mixture, and we rewrite the rate equation as

$$\frac{\alpha d(1/[OH])}{d\tau} = A \frac{\rho}{\rho_0} [M] (k_1 + \alpha k_2). \quad (15)$$

Equation (15) has been cast in this form in anticipation of finding the disappearance of OH to be effectively second order in OH and of determining the slope of an approximately linear plot of  $1/[OH]$  versus  $\tau$  from each experiment.

This slope represents, of course, only an average effective second order rate coefficient. Its detailed

TABLE I. Composition of experimental mixtures.

Designation	% $H_2$	% $O_2$	% Ar
R-1	4.03	1.00	94.97
R-2	2.02	0.50	97.48
R-3	8.07	1.00	90.93

<sup>21</sup> S. S. Penner, *Chemistry Problems in Jet Propulsion* (Pergamon Press, New York, 1957), Sec. 72.

<sup>22</sup> W. E. Kaskan and G. L. Schott, *Combust. Flame* **6**, 73 (1962).

TABLE II. Summary of experimental results.\*

Mix	Shock velocity (obs)	[OH]×10 <sup>6</sup> (obs)		$d(1/[OH])$		T (calc)	[M]×10 <sup>3</sup> (calc)	$\alpha \times 10^3$ (calc)	$(k_1 + \alpha k_2) \times 10^{-8}$
		initial	final	$d\tau \times 10^{-9}$	[OH]×10 <sup>6</sup> (calc)				
R-1	1.226	5.2	2.5	0.80	6.64	1546	8.84	4.49	10.5
R-1	1.232	5.1	2.2	0.68	6.87	1560	8.87	4.65	9.3
R-1	1.251	7.2	2.4	0.75	7.56	1599	8.92	5.13	11.3
R-1	1.396	14.2	4.5	0.42	13.78	1921	9.31	9.71	12.1
R-1	1.408	13.0	3.5	0.37	14.35	1949	9.34	10.15	11.4
R-1	1.417	16.9	4.1	0.37	14.81	1972	9.36	10.50	11.8
R-1	1.200	6.9	1.8	1.47	11.57	1494	17.52	3.89	8.4
R-1	1.223	11.0	1.2	1.39	13.12	1541	17.67	4.43	9.0
R-1	1.275	14.0	1.4	1.05	16.97	1651	17.99	5.79	9.0
R-1	1.293	17.1	2.2	1.09	18.40	1689	18.09	6.31	10.2
R-1	1.385	26.7	2.9	0.88	26.54	1896	18.58	9.33	12.3
R-1	1.388	28.2	2.9	0.74	26.80	1903	18.59	9.42	10.4
R-1	1.196	13.4	0.6	3.23	22.58	1485	34.99	3.80	9.0
R-2	1.209	3.4	2.1	0.65	3.27	1543	8.79	4.42	7.0
R-2	1.345	6.6	2.8	0.55	6.04	1844	9.15	8.52	12.4
R-2	1.362	6.4	3.5	0.28	6.44	1885	9.19	9.14	6.8
R-2	1.381	13.6	2.5	0.64	13.80	1931	18.46	9.86	8.6
R-2	1.184	5.9	0.5	3.53	8.21	1490	25.21	3.81	11.1
R-3	1.247	1.8	0.6	2.31	2.20	1525	8.97	1.26	6.2
R-3	1.253	2.1	0.7	2.76	2.28	1537	8.99	1.31	7.6
R-3	1.279	2.4	0.7	2.35	2.69	1589	9.07	1.53	7.3
R-3	1.408	3.9	1.1	1.56	5.32	1863	9.43	2.97	8.2
R-3	1.409	4.6	1.4	1.37	5.35	1866	9.44	2.99	7.3
R-3	1.417	4.9	1.3	1.63	5.55	1884	9.46	3.10	8.9
R-3	1.185	2.2	0.3	7.84	2.85	1405	17.53	0.835	7.8
R-3	1.212	2.7	0.4	5.64	3.47	1457	17.72	1.01	6.4
R-3	1.217	2.7	0.4	4.91	3.59	1466	17.75	1.04	5.7
R-3	1.396	6.9	1.1	2.66	10.09	1838	18.81	2.82	6.7
R-3	1.399	7.2	1.0	2.74	10.21	1843	18.82	2.85	7.0
R-3	1.348	8.7	0.4	4.63	12.79	1733	29.92	2.23	6.0
R-3	1.229	4.7	0.4	11.1	7.76	1488	35.65	1.12	6.8

\* Concentrations are in moles per liter, times in seconds, temperatures in Kelvin degrees, and velocities in kilometers per second.

interpretation in terms of the elementary rate coefficients  $k_1$  and  $k_2$  involves determination of  $\alpha$ ,  $A$ ,  $(\rho/\rho_0)$ , and  $[M]$  at a point in the course of the reaction where the apparent line is tangent to the true curve. This point has been selected, somewhat arbitrarily, as that at which the ratio of the total to the original total mole number,  $n/n_0 = \Sigma n_i / \Sigma n_{i0}$ , is equal to 0.9995. In Mixtures R-1 and R-3 this corresponds to 5% of the total recombination necessary to quantitatively convert the original  $O_2$  to  $H_2O$  with no formation of  $H$ ,  $OH$ , or  $O$ . In mixture R-2, this same figure represents 10% recombination.

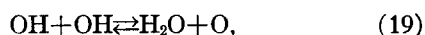
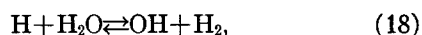
Computation of the conditions at selected values of  $n/n_0$  was done assuming equilibrium with respect to all reactions except those which affect  $n/n_0$ . Implicit in these computations are the relationships:

$$\alpha = [OH]/[H] = K_{18}[H_2O]/[H_2], \quad (16)$$

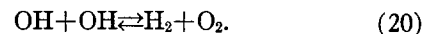
and

$$\beta = ([O] + [O_2])/[OH]^2 = K_{19}/[H_2O] + K_{20}/[H_2], \quad (17)$$

where  $K_{18}$ ,  $K_{19}$ , and  $K_{20}$  are the equilibrium constants for the reactions



and



It was established at the outset that the various parameters of interest were satisfactorily linear in  $n/n_0$  over the range between  $n/n_0 = 1.0000$  and final equilibrium, and final computations for each experiment were actually done for  $n/n_0$  equal to 1.000 and 0.999. The values of  $[M]$ ,  $\alpha$ , and  $(\rho/\rho_0)$  which appear in Eq. (15) were taken as the means of these two computations. Evaluation of  $A$  utilized the mean value of the product  $\beta[OH]$  and approximate logarithmic derivatives obtained from the finite differences between the  $n/n_0 = 1.000$  and 0.999 computations.

## RESULTS

Experiments have been done with three different gas mixtures, whose compositions are given in Table I. The results of 31 experiments in the temperature range  $1400^\circ \leq T \leq 2000^\circ K$  are assembled in Table II. In these experiments the plots from which

$$\frac{d(1/[OH])}{d\tau}$$

was determined were approximately straight over the entire interval plotted, which in most cases was from



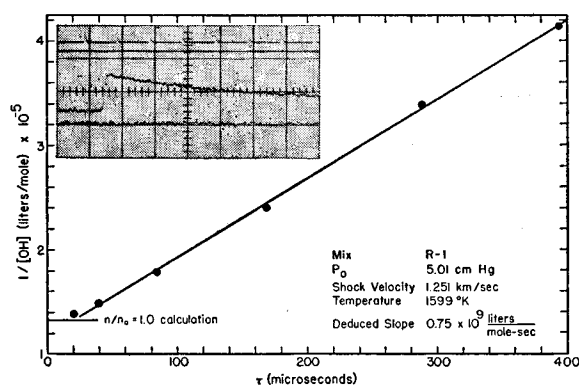


FIG. 1. Plot of  $1/[\text{OH}]$  vs  $\tau$  for one experiment, with the oscilloscope record of ultraviolet light transmission from which it was derived. Experimental conditions are recorded in the third line of Table II. Timing mark interval is 100  $\mu\text{sec}$ .

about 50 to about 500  $\mu\text{sec}$  after passage of the shock front. During this period  $[\text{OH}]$  fell from the values given in Column 3 to those given in Column 4. Figure 1 shows this plot for one experiment, and includes the oscilloscope record from which  $[\text{OH}]$  and  $\tau$  were measured. Column 5 in Table II contains the slopes derived from the plots. Columns 6 and 7 contain the values of  $[\text{OH}]$  and temperature computed from the initial data and the shock velocity for each experiment on the basis of equilibrium with respect to all reactions except dissociation-recombination reactions and  $n/n_0 = 1.0000$ .  $[M]$  and  $\alpha$  evaluated for  $n/n_0 = 0.9995$  are listed in Columns 8 and 9 of Table II.  $(\rho/\rho_0)$  was invariably between 3.2 and 3.6, and the factor  $A$  varied systematically from 1.7 to 1.0 as  $\alpha$  varied from 0.01 to 0.1.

The derived values of  $k_1 + \alpha k_2$  given in the last column of Table II were obtained from the measured slopes in column 5 by multiplication by the factor  $\alpha \rho_0 / \rho [M] A$ . These are plotted against  $\alpha$  in Fig. 2, with different

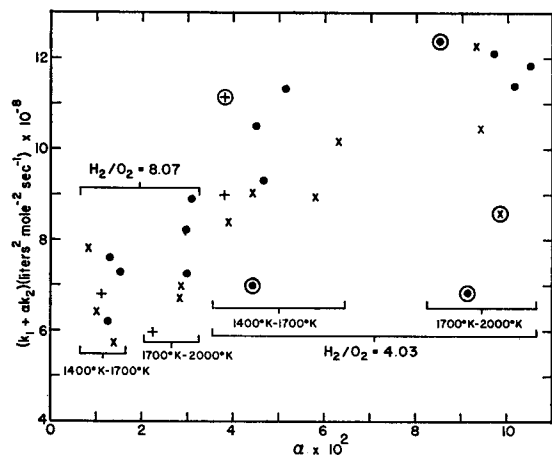


FIG. 2. Plot of  $(k_1 + \alpha k_2)$  vs  $\alpha$  covering all experimental conditions investigated.  $\bullet$ ,  $P_0 = 5$  cm Hg;  $\times$ ,  $P_0 = 10$  cm Hg; and  $+$ ,  $P_0 > 10$  cm Hg. Circled points, 0.5%  $\text{O}_2$ ; uncircled points, 1%  $\text{O}_2$ .

ranges of experimental conditions distinguished. To establish a dependence of  $k_1$  or  $k_2$  upon temperature, it would be necessary to determine that the two groups of points in the higher temperature range define a different line from that defined by the two low temperature groups. This cannot be done. Among the uncircled points between  $\alpha = 0.02$  and  $\alpha = 0.07$ , those at higher initial pressures appear to lie systematically lower than those at lower pressures. However this trend is not borne out by the other sets of experiments.

Table III presents values of  $k_1$  and  $k_2/k_1$  derived by linear least squares fitting of the entire set of values of  $k_1 + \alpha k_2$  in Table II and the indicated subsets thereof. From this analysis we conclude that  $k_1$  in an atmosphere consisting primarily of argon is  $6 \pm 1 \times 10^8 \text{ liter}^2 \text{ mole}^{-2} \cdot \text{sec}^{-1}$  between 1400° and 2000°K, and that  $k_2/k_1 \approx 10 \pm 5$  under these same conditions.

TABLE III. Extraction of individual rate coefficients from groups of experiments.

$T$ range (°K)	$[M]$ range mole/liter $\times 10^3$	Mixtures	No.	$k_1$ liter <sup>2</sup> mole <sup>-2</sup> $\cdot \text{sec}^{-1}$ $\times 10^{-8}$		$k_2/k_1$
1400-2000	8-36	All	31	6.6		7.1
1400-1700	8-36	All	17	6.1		11.4
1700-2000	9-30	All	14	5.9		8.5
1400-2000	8-36	$R-1$	13	7.6		5.3
1400-2000	8-35	$R-3$	13	6.2		7.0
1400-1700	8-10	$R-1, R-3$	6	5.6		17.8
1400-1700	17-19	$R-1, R-3$	7	6.1		9.5
1700-2000	9-10	$R-1, R-3$	6	6.6		7.7
1700-2000	17-19	$R-1, R-3$	4	4.9		14.0

## DISCUSSION

### Assumptions

To be sure, significant departure of  $\alpha$  from the assumed partial equilibrium value of  $K_{18}[\text{H}_2\text{O}]/[\text{H}_2]$  would lead to serious error in the rate coefficients deduced. However, the available data<sup>23</sup> on the rates of the bimolecular reactions paths by which this equilibrium is approached indicate that  $\alpha$  does not depart from its ideal value by more than a few percent under the conditions of the present measurements. Departure of  $[\text{O}]$  and  $[\text{O}_2]$  from their assumed equilibrium relationship to  $[\text{OH}]$  would be less serious in the rich mixtures studied here. The fact that the values of  $[\text{OH}]$  in Column 3 of Table II approximate but generally do not exceed those in Column 6 also supports the partial equilibrium assumption.

The value of  $k_2/k_1$  obtained here is dependent upon certain assumptions made in its deduction, not the least of which is that Reactions (1) and (2) are com-

<sup>23</sup> F. Kaufman and F. P. Del Greco, Symp. Combust. 9th Cornell Univ. Ithaca, N. Y. 1962, 659 (1963).

pletely responsible for the dependence of the weighted sum of rate coefficients,  $(k_1 + \alpha k_2)$ , upon  $\alpha$ . Now combination of Eqs. (16) and (17) shows that the concentrations of O and O<sub>2</sub> in partial equilibrium are proportional to  $\alpha$  and  $\alpha^2$ , respectively. Should additional reactions involving OH, O, and/or O<sub>2</sub> contribute significantly to the recombination rate, the increased dependence of the rate on  $\alpha$  would appear as an increase in  $k_2$ . Moreover, since [O] and [O<sub>2</sub>] are much larger in proportion to [H] early in the course of recombination than in the much later stages of the reaction studied in flames, our experiments are more susceptible of such an effect. Yet the ratio  $k_2/k_1$  we observe is smaller than that reported in flame gases, which indicates that there is no large contribution from neglected recombination paths. This conclusion applies equally well to purely collisional processes and to the potentially radiative processes which proceed through the electronically excited OH intermediate responsible for the chemiluminescence observed by others.<sup>20</sup>

Another assumption which affects the apparent ratio  $k_2/k_1$  is that the total gas concentration  $[M]$  may be substituted for  $[M_1]$  and  $[M_2]$  in Eq. (14). This substitution is valid provided that both  $[M_1]$  and  $[M_2]$  are proportional to  $[M]$  over the range of composition of the gas acting as third body. Since all three experimental mixtures contained over 90% Ar, no large error should be introduced by this assumption. However since H<sub>2</sub> is apparently several times more effective than Ar as a third body in Reaction (1), and since H<sub>2</sub> comprised about 5% of the gas (after formation of about 2% H<sub>2</sub>O and 2% H) in Mixture R-3 and only about 1.2% in Mixture R-1, an artificial lowering of  $k_2/k_1$  by perhaps 20% probably resulted from this systematic variation of the third-body composition with  $\alpha$ .

### Gas-Dynamic Instability

Nine additional experiments were attempted at temperatures between 1100° and 1300°K. These yielded apparent rate coefficients which scattered between 50% and 200% of those found above 1400°K. In several of these experiments, particularly those at higher densities, there were undulations of the OH absorption record and other indications of spinlike instability in the flow behind the shock wave. Investigation of this behavior is outside the scope of the present paper. However it may well be that such instabilities are in fact present in the higher temperature experiments, but their amplitude is evidently small enough and/or their scale fine enough not to disrupt the recombination kinetics dramatically. White<sup>24</sup> has examined Mixture R-3 by flash interferometry in an 8.25-cm-square shock tube and found indications of mildly nonlaminar flow under the density and temperature conditions of

<sup>24</sup> D. R. White, General Electric Research Laboratory (private communication, July 1964).

TABLE IV. Values of  $k_1^M$ , in (mole/liter)<sup>-2</sup> sec<sup>-1</sup>, at different temperatures.

<i>M</i>	Temperature				
	300°K	1072°K <sup>a</sup>	1400°K <sup>b</sup>	1700°K	3500°K
H <sub>2</sub>	9×10 <sup>9</sup> <sup>c</sup>	3×10 <sup>9</sup>	8.6×10 <sup>9</sup>	2×10 <sup>9</sup> <sup>d</sup>	8×10 <sup>8</sup> <sup>e</sup>
H	1×10 <sup>10</sup> <sup>f</sup>			5×10 <sup>9</sup> <sup>d</sup>	5×10 <sup>9</sup> <sup>g</sup>
H <sub>2</sub> O		1.8×10 <sup>9</sup>	≤3.6×10 <sup>9</sup>	2×10 <sup>9</sup> <sup>d</sup>	
Ar	9×10 <sup>9</sup> <sup>h</sup>			4×10 <sup>8</sup> <sup>i</sup>	2×10 <sup>8</sup> <sup>j</sup>

<sup>a</sup> From Ref. 3, converted to present units and definitions by multiplication by  $(N^2/2 \times 10^9)$ , where  $N$  is Avogadro's number.

<sup>b</sup> From Ref. 4, converted as in Footnote a.

<sup>c</sup> Consensus value based on values of: 9×10<sup>9</sup>, from Ref. 25; 9×10<sup>9</sup>, from Ref. 26, converted as in a; 1.2×10<sup>10</sup>, from Ref. 27; and 5×10<sup>9</sup>, from Ref. 28, converted by division by 2×10<sup>9</sup>.

<sup>d</sup> Estimated from values in this table at other temperatures.

<sup>e</sup> Consensus value based on values of the ratio of the dissociation rate coefficient to the equilibrium constant; 8.6×10<sup>9</sup>, from Ref. 29; 7×10<sup>9</sup>, from Ref. 30; 2.1×10<sup>9</sup>, from Ref. 31; and 1.3×10<sup>9</sup>, from Ref. 32, converted via Ref. 31.

<sup>f</sup> Tenuous value, see Ref. 28.

<sup>g</sup> Consensus value based on values of: 2.9×10<sup>9</sup>, from Ref. 29; 9×10<sup>9</sup>, from Ref. 30; 1.4×10<sup>10</sup>, from Ref. 31; and 3×10<sup>9</sup>, from Ref. 32 via Ref. 31.

<sup>h</sup> Tenuous value, from  $k_1^{Ar} = k_1^{H_2}$ , Ref. 33.

<sup>i</sup> Deduced herein.

<sup>j</sup> Consensus value based on values of: 4.3×10<sup>8</sup>, from Ref. 29; 1.7×10<sup>8</sup>, from Ref. 30; and 2.1×10<sup>8</sup>, from Ref. 31.

our experiments. The perturbation in the flow was most pronounced in the interferogram at the highest initial pressure examined, 15 cm Hg.

### Extraction of $k_1^{Ar}$

To reduce the value of  $k_1$  determined here to the specific rate coefficient for Ar as third body, it is necessary to subtract the contributions made to  $k_1$  by the small but significant percentages of H<sub>2</sub>, H, and H<sub>2</sub>O present in our mixtures. These contributions are not known precisely, but they can be estimated from the values of  $k_1^{H_2}$  and  $k_1^{H_2O}$  reported in the flame investigations and the other data available from room temperature recombination rate measurements and the dissociation rate measurements made above 3000°K. Such data are assembled in Table IV,<sup>25-33</sup> which serves to illustrate the temperature dependence of  $k_1^M$  for the various third bodies and the level of agreement among different determinations. Save for the value at 1400°K, the behavior of  $k_1^{H_2}$  with temperature is smooth and reasonable, approximating proportionality to  $T^{-1}$ .  $k_1^H$  is less well established, but if its magnitude is as great as indicated, its contribution to our rate

<sup>25</sup> C. B. Kretschmer and H. L. Petersen, J. Chem. Phys. **39**, 1772 (1963).

<sup>26</sup> L. I. Avramenko and R. V. Kolesnikova, Izvest. Akad. Nauk SSSR, Otd. Khim. Nauk **1961**, 1971 (1961).

<sup>27</sup> T. C. Marshall, Phys. Fluids **5**, 743 (1962).

<sup>28</sup> I. Amdur, J. Am. Chem. Soc. **60**, 2347 (1938).

<sup>29</sup> J. P. Rink, J. Chem. Phys. **36**, 262 (1962).

<sup>30</sup> E. A. Sutton, J. Chem. Phys. **36**, 2923 (1962).

<sup>31</sup> R. W. Patch, J. Chem. Phys. **36**, 1919 (1962).

<sup>32</sup> W. C. Gardiner, Jr., and G. B. Kistiakowsky, J. Chem. Phys. **35**, 1765 (1961).

<sup>33</sup> L. Farkas and H. Sachsse, Z. Physik. Chem. (Leipzig) **B27**, 111 (1934).



measurements is significant.  $k_1^{\text{H}_2\text{O}}$  is not uniquely determined from flame measurements,<sup>4</sup> and there are no room temperature or dissociation rate measurements in wet systems. However the two values reported are in reasonable agreement, and they place an upper limit on  $k_1^{\text{H}_2\text{O}}$  which is comparable to  $k_1^{\text{H}_2}$ . If one formulates  $k_1$  for mixture R-3, in which the mole fractions of  $\text{H}_2$ ,  $\text{H}$ , and  $\text{H}_2\text{O}$  are about 0.05, 0.02, and 0.02, respectively, at partial equilibrium with no recombination, one obtains:

$$k_1 = 0.91k_1^{\text{Ar}} + 0.05k_1^{\text{H}_2} + 0.02k_1^{\text{H}} + 0.02k_1^{\text{H}_2\text{O}} \\ = 6 \times 10^8 \text{ liter}^2 \text{ mole}^{-2} \cdot \text{sec}^{-1}.$$

Substitution of the estimated values into the last three terms shows that these "corrections" amount to 36% of  $k_1$ , and yields  $k_1^{\text{Ar}} = 4 \times 10^8 \text{ liter}^2 \text{ mole}^{-2} \cdot \text{sec}^{-1}$ . Estimated uncertainty in this value is  $\pm 2 \times 10^8$ . Such a value is in reasonable relationship to the fairly well

established value of the ratio of the dissociation rate coefficient to the equilibrium constant near 3500°K.

### CONCLUSION

It should be stated in conclusion that in the design of the experiments, the determination of individual rate coefficients  $k_1^M$  or  $k_2^M$  was subsidiary to the testing of the reaction rate equation Eq. (15) over a substantial range of  $[M]$ ,  $\alpha$ , and  $[\text{OH}]$ . We believe that this rate equation is satisfactorily established by the data presented, and that the feasibility of measurement of slow, mildly exothermic recombination reaction rates in shock waves is demonstrated.

### ACKNOWLEDGMENTS

The authors acknowledge gratefully the participation of John G. Williamson and James L. Young in the performance of the experiments and Michael P. Eastman in the measurement of the photographic records.

## On Spin Relaxation

ROBERT L. FULTON\*

*Conant Chemical Laboratory, Harvard University, Cambridge, Massachusetts*

(Received 4 June 1964)

A rigorous formulation of spin relaxation which allows physical insight into the nature of the relaxation process, allows higher-order approximations than hitherto made to be easily formulated and which gives a starting point for a discussion of long correlation times is given. Two approximations are considered in turn, both based on the shortness of the correlation time for the heat bath. One is shown to lead to the usual density matrix formulation, the other to the method of Argyres and Kelley. The explicit solutions of the resulting equations are found in the case of a constant magnetic field plus a perpendicular rotating field when the heat bath displays two-dimensional rotational symmetry. The differences between the two approximations are noted, giving a limit on the validity of both. The effect of initial correlation between the heat bath and spin is incorporated into the theory.

### I. INTRODUCTION

**T**HEORIES of spin relaxation have been developed by a number of authors.<sup>1-4</sup> In general these have fallen into two categories, those based on an explicit examination of the time development of the density matrix,<sup>1,3,4</sup> with a separation of the matrix into a reduced density matrix which completely describes the spin system and the rest describing the heat bath and correlations between the heat bath and spin system,<sup>5</sup>

and those based on an examination of the linear response of the spin system to an external field.<sup>2</sup>

Most of these theories, especially those based directly on the density matrix, have suffered a number of defects.<sup>6</sup> These are briefly that the theories are restricted to a treatment of cases in which the correlation time of the heat bath  $\tau_c$  is much shorter than a typical relaxation time of the spin system, the procedure necessary to extend the treatment so as to include higher-order terms is not clear, the restriction to times sufficiently short that the lowest order of perturbation theory is valid, yet sufficiently long that the correlation functions of the bath vanish,<sup>7</sup> and the

\* Society of Fellows, Harvard University.

<sup>1</sup> F. Bloch, *Phys. Rev.* **102**, 104 (1956).

<sup>2</sup> R. Kubo and K. Tomita, *J. Phys. Soc. Japan* **9**, 888 (1954).

<sup>3</sup> See A. Abragam, *Principles of Magnetic Resonance* (Harper and Row Publishers, New York, 1963), for a good review of the density matrix approach.

<sup>4</sup> P. N. Argyres and P. L. Kelley, *Phys. Rev.* **134**, A98 (1964).

<sup>5</sup> Reference 4 gives both a concise and precise formulation of this approach. See also M. Lax, *J. Phys. Chem. Solids* **25**, 487 (1964).

<sup>6</sup> Many of the objections cited in this paragraph do not apply to the formal development of the theory presented in Ref. 4. The theory as applied to special cases is restricted to  $\tau_c$  "sufficiently" short, in spite of counter claims by the authors. This is brought out in the latter part of this paper.

<sup>7</sup> See Ref. 3, pp. 282, 286.