again the absolute magnitudes of the solvent effects are reduced, in two cases—phenetole and chlorobenzene—almost to zero. On the whole, however, Smith's treatment gives values for the moments which are further from the true vapor values than Sugden's. On the other hand it does enable a very much larger body of experimental data to be rationalized than can be achieved by employment of equation 5. The plots of $P_{2\infty}$ cor. against volume polarization of the solvent approximate very closely to straight lines and in no case considered, even when highly polar solvents are used, do any of the experimental points lie markedly off these lines. This fact, combined with the improved agreeement between $\mu_{soln.}$ and μ_{vapor} shows that the treatment is one of considerable value.

We now consider the applicability of Goss's treatment of the data obtained in carbon tetrachloride solutions. The orientation polarizations of the five solutes are recorded in column (d) of Table III. It is seen that once again the values obtained are higher than those by the conventional method, and that again the absolute magnitudes of the solvent effects are reduced. Indeed, with the one exception of benzonitrile, it is seen that the agreement between $\mu_{soln.}$ and μ_{vapor} is now in general better than that obtained either by Sugden's or Smith's methods. With all the solutes, however, there is still an appreciable solvent effect.

It cannot therefore be said that any of the treatments that have been discussed are entirely satisfactory in translating the solution data into the true dipole moment of the solute considered. The conventional method leads to values which are too low, the other methods generally to values which are too high.

In view of this fact it has seemed reasonable to try the effect of averaging the polarization values obtained by the four different treatments. These mean values are given in column 5 of Table III and the dipole moments calculated therefrom in column 6.

When these are compared with the true vapor values, given in column 7 of the same table, it is seen that the agreement is in all cases remarkably good. In no instance do the figures in column 6 and 7 differ by more than 0.09 Debye unit. The maximum error involved in taking the value of the moment from column 6 is about 2% (for nitrobenzene), the average error is about 1%. This is considered very reasonable.

Attempts to improve the agreement between the figures in columns 6 and 7 by including in the former values obtained by use of a number of other solvent effect treatments, e.g., Onsager's,[17] and Guggenheim's,[18] were unsuccessful. Such inclusions in general led to poorer agreement.

It is therefore concluded that a likely value of a dipole moment will be obtained from solution data by averaging the values derived from the conventional method and the three solvent effect treatments discussed. Further work, however, will be needed to confirm this finding.

Diffusion Kinetics of the Photochemical and Thermal Dissociation-Recombination of Trihalide Ions[1]

BY J. C. ROY, W. H. HAMILL AND R. R. WILLIAMS, JR.

A diffusion equation for dissociation–recombination in the non-steady state region is applied to the photodissociation of Br_3^- and I_3^-, using Mn(II) as a radical scavenger. The efficiency of oxidation of Mn(II) is enhanced by additional X^-. If $X_3^- \rightarrow X_2^-\cdot + X\cdot$, the effect of additional X^- is attributable to $X^- + X\cdot \rightarrow X_2^-\cdot$ which hinders recombination. The thermal dissociation of iodine, in the presence of Mn(II) and of I^-, exhibits a similar dependence upon concentration of I^- but different kinetics may apply.

In the preceding paper of this series[2] yields of radiohalogen following neutron capture in several liquid alkyl halides as a function of the concentration of added free halogen were shown to be describable in terms of diffusion controlled dissociation-recombination in a two particle system. The equation appearing below was derived, as an extension of the work of Samuel and Magee,[3] to describe the probability of recombination W of two free radicals as modified by a competing reaction with a reactive solute at mole fraction X; the primary dissociation results in an initial mean separation $\bar{R}_0 = n_0^{1/2} L$, where n_0 is the number of displacements of mean free path L, in terms of an equivalent fictitious separation by random walk. Also $\gamma = Ld^{-1}$ and $\rho_0 = \bar{R}_0 d^{-1}$.

$$-\ln(1 - W_\infty(X))(1 - W_0(X))^{-1} =$$
$$\sigma P_1 [\pi L^2 (2\pi n_0)^{1/2}]^{-1}[1 - (\pi n_0 P_2 X)^{1/2}]$$
$$= P_1[2.51\gamma\rho_0]^{-1} - P_1 P_2^{1/2}[1.41\gamma^2]^{-1}X^{1/2} \quad (1a)$$

$$-\log(1 - W_\infty(X)) = -[\log(1 - W_0(X)) + P_1(5.75\gamma\rho_0)^{-1}] - P_1 P_2^{1/2}[3.24\gamma^2]^{-1}X^{1/2} \quad (1b)$$
$$= \beta - \mu X^{1/2}$$

In equation 1a, $\sigma = \pi d^2$ is the collision cross section for recombination occurring with probability P_1 per

(1) From the doctoral dissertation of Jean-Claude Roy, University of Notre Dame, June, 1954. Presented at the 126th meeting of the American Chemical Society, New York, September, 1954. This work was been supported in part by a grant from the Atomic Energy Commission under contract At(11-1)-38.
(2) J. C. Roy, R. R. Williams. Jr., and W. H. Hamill, THIS JOURNAL, **76**, 3274 (1954).
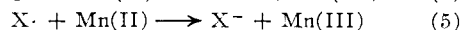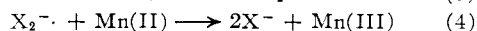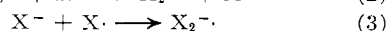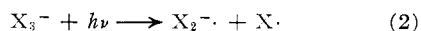(3) A. H. Samuel and J. L. Magee, *J. Chem. Phys.*, **21**, 1080 (1953).

encounter; P_2 is the probability of reaction per encounter between a fragment of dissociation and the reactive solute at mole fraction X.

We may compare the preceding equation with that of Wijsman.[4] Equating his λ, the ratio of mean free path for scattering to mean free path for absorption, to our P_2X and for the case that $\lambda << 1$, Wijsman's treatment leads to a predicted probability of recombination varying as

$$W_\infty(X) = W_\infty(0) \exp(- \sqrt{3n_0P_2X})$$

in terms of the present symbols. Noyes[5] also finds that the probability of recombination varies as $X^{1/2}$. Pending completion of a study of the theory of diffusion recombination now in progress in these laboratories[6] we shall continue using equation 1.

Results from studies of Szilard–Chalmers reactions[2] gave the rather plausible results $\bar{R}_0/d \cong 3$, $L/d \cong 0.5$ provided that $P_1 = P_2 = 1$. It cannot be claimed, however, that this evidence is very convincing because of the complexity of the processes involved. More nearly suitable data in the chemical literature are, unfortunately, scarce. The careful measurements of Rutenberg and Taube[7] for the photolysis of Br_3^-, which show a dependence of quantum yield for $Mn(II)$ oxidation increasing with added Br^-, appear to furnish an appropriate example if one adopts the mechanism

$$X_3^- + h\nu \longrightarrow X_2^- \cdot + X \cdot \qquad (2)$$
$$X^- + X \cdot \longrightarrow X_2^- \cdot \qquad (3)$$
$$X_2^- \cdot + Mn(II) \longrightarrow 2X^- + Mn(III) \qquad (4)$$
$$X \cdot + Mn(II) \longrightarrow X^- + Mn(III) \qquad (5)$$

Reactions 3, 4 and 5 are assumed to occur at every, or nearly every, encounter; reaction 5 is important only in the absence of appreciable concentration of halide ion since the concentration of $Mn(II)$ was always $ca.$ 10^{-3} M. Subject to corrections for photodissociation of Br_2 and for salt effect we find that these results are interpretable by equation 1, as discussed below.

As a supplementary test of the diffusion equation we have chosen the photoreduction of I_3^- by $Mn(II)$, continuing the work of Rutenberg and Taube.[7] This system has the advantage that $K_{X_3^-}$ is much larger for iodine than for bromine; no correction is necessary for the photoreduction of I_2 even at rather small concentrations of iodide and there is no evidence of salt effect within the limited range of ionic strengths involved here. This system, whose reaction mechanism is assumed to be the analog of that for manganous–tribromide, has been studied at 19, 28 and 35° at 3650 Å. and at 4360 Å. The corresponding thermal reaction has been measured at 60°.

Experimental

The chemistry of the manganous–trihalide systems has been described; our analytical procedure was substantially that previously used.[7,8]

Apparatus.—A 1000-watt, high pressure mercury lamp (General Electric A-H6) with accessory equipment provided

a collimated light beam. Corning filters 3389 with 5113 and 7380 with 5860 were used to isolate the regions at 4360 Å. and at 3650 Å. The photolytic reaction cell was a Pyrex cylinder with optically flat windows 35 mm. in diameter, 29 mm. long. During a run the cell was mounted in a thermostated aluminum cylinder. The solution was stirred vigorously during photolysis. Extinction coefficients were measured, when not otherwise available, with a Beckman DU spectrophotometer. Conventional apparatus was used for thermal reaction rate measurements.

Procedure.—Two 15-ml. portions of each reaction mixture for photolysis were measured, one for photolysis and the other as a blank for the dark reaction. Correction for the dark reaction did not exceed 10% and averaged 5% of the photochemical run.

Light intensity was monitored with a photocell which was compared in turn with the system manganous–tribromide, 0.2 M in bromide, at 19°. This choice of actinometer had a considerable analytical advantage. The quantum yield, defined as molecules of iodine reacting per quantum absorbed, is simply the known quantum yield for the actinometer multiplied by the ratio of the volumes of thiosulfate required to titrate[7,8] actinometric and reaction mixtures.

For thermal rate measurements, 200 ml. of reaction mixture was deaerated with a rapid stream of nitrogen for 20 min.; the stirred solution was thermostated at 60°, maintaining a slow stream of nitrogen. Portions were expelled through a siphon into a chilled receiver and 25-ml. samples taken for analysis; all measurements of concentration were relative to the first analysis; other samples were analyzed beginning 1–2 hr. later.

Results and Discussion

In the photoöxidation of $Mn(II)$ by triiodide ion it was found that the quantum yield is independent of light intensity; is independent of the concentration of $Mn(II)$ in the range used; is independent of the concentration of iodine; depends upon wave length; depends upon temperature; depends greatly upon concentration of iodide ion; is not affected by moderate changes in ionic strength involved in this work. These facts are qualitatively similar to those for the manganous tribromide system except for the small salt effect in the latter case.

Reaction 2 may be followed, according to the present treatment, by primary recombination (Franck–Rabinowitch cage effect) and this would be difficult to distinguish from an excitation–de-excitation sequence as postulated for the manganous–tribromide system.[7] If de-excitation occurs within a time short compared to a diffusive displacement its effect would be included in $W_0(X)$ of equation 1, the probability of recombination (nondissociation) at zero time. Of those radicals which escape primary recombination, a significant fraction undergo diffusive secondary recombination with their original partners[9a,b]; Noyes[9b] proposes "geminate recombination" to designate the combined effect. The rest eventually enter the steady state.[10] Such radicals, for the reactions under consideration, are efficiently removed by even rather small concentrations of $Mn(II)$ since there is no important competing process. At $ca.$ 10^{-4} mole fraction $Mn(II)$ moderate variations in its concentration are without effect; the concentration is not

(4) R. A. Wijsman, Bull. Math. Biophys., 14, 121 (1952).

(5) R. M. Noyes, forthcoming publication.

(6) J. L. Magee and L. Monchick, private communications.

(7) A. C. Rutenberg and H. Taube, THIS JOURNAL, 73, 4426 (1951).

(8) A. Rutenberg and H. Taube, ibid., 72, 5561 (1950).

(9) (a) R. M. Noyes, J. Chem. Phys., 22, 1349 (1954). (b) R. M. Noyes, forthcoming publication.

(10) Quite apart from any consideration of the details of the present treatment it is evident that unmodified steady state methods are not applicable to reaction systems in which there is an appreciable probability that any reagent may intervene in the secondary recombination of dissociation partners. Instances to the contrary cannot be better than approximations.

large enough to interfere with primary or secondary recombination nor so small as not to result in capture of all radicals which escape both primary and secondary recombination.

The increase in quantum yield, Φ, with increase of halide ion as recombination inhibitor (see Fig. 1) is attributed to intervention of reaction 3 prior to reversal of reaction 2 by diffusion.[11] Recombination of two $X_2^-\cdot$ radical ions is effectively prevented by coulombic repulsion. A decrease in P_1 by a factor of 10 is sufficient for such an effect.[12] The function of Mn(II) as scavenger,[13] for our purpose, is to remove all $X_2^-\cdot$ and $X\cdot$ which escape secondary recombination; the Mn(III) produced is the measure of non-recombination, $1 - W_\infty(X)$. The extent of primary recombination is very unlikely to be affected by these small amounts of solute, i.e., $W_0(0) = W_0(X)$.
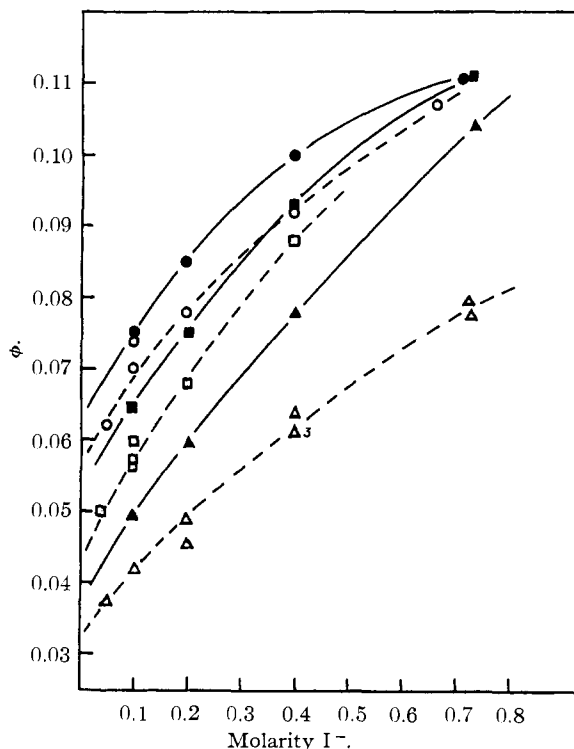

Fig. 1.—Quantum yield for reduction of I_2 by Mn(II) with added I^-: continuous curves, 3650 Å.; broken curves, 4360 Å.; circles, 35°, squares 28°, triangles 19°. The index "3" denotes three overlapping measurements.

To test equation 1b replace the terms $1 - W_\infty(X)$ and $1 - W_\infty(0)$, the probabilities of non-recombination of original dissociation partners after infinite time with and without solute, respectively, by the corresponding quantum yields. The results of our photochemical measurements with manganous-triiodide ions, expressed as log Φ vs. $X_I^{1/2}$ appear in Fig. 2. The intercept is taken to represent non-re-

(11) Reaction 3 was proposed independently by R. M. Noyes, ref. 9a.

(12) By equation 1b this would be equivalent to changing P_2 by a factor of 10^{-2}. See Fig. 2, ref. 2.

(13) In terms of the quantum yield for halogen reduced, any other reasonably efficient scavenger of radicals could be used, as will appear. Similarly, other efficient inhibitors of recombination would give results comparable to Br^- or I^- for the systems being considered.

combination for photolysis of triiodide ion rather than of iodine since it is obtained by extrapolation from concentrations of iodide ion at which only negligible amounts of free iodine were present.
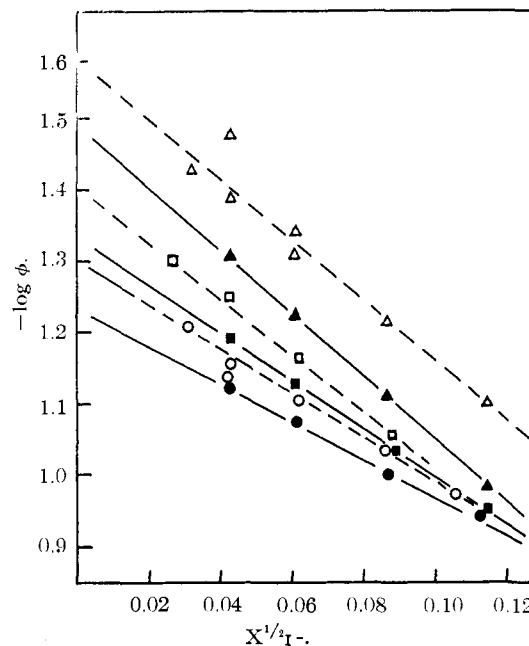

Fig. 2.—Logarithm of quantum yield for reduction of I_2 by Mn(II) with square root of mole fraction of I^-; continuous curves 3650 Å.; broken curves 4360 Å.; circles 35°, squares 28°, triangles 19°.

In order to apply this method to the results of Rutenberg and Taube[7] for manganous–tribromide it was first necessary to correct all quantum yields for light absorbed by free bromine at the two lower concentrations of bromide ion using

$$\Phi' = [\Phi_{Br_3^-} - (1 - f)\Phi_{Br_2}]f^{-1}$$

$\Phi_{Br_3}^-$ and Φ_{Br_2} are observed quantum yields with and without added bromide and f is the fraction of light absorbed by tribromide, based upon the extinction coefficients of Griffith, et al.[14] Finally, Φ' was divided by $(1 - 8.3X_{Br^-})$ to correct empirically for an observed salt effect. Values of Φ so obtained appear in Fig. 3.

To simplify the problem of examining the results of these graphs, as summarized in Table I, let $W_0(X) = 0$ in all cases. This choice is not evidently implausible and is, at the worst, a tolerable approximation. The temperature dependence of the intercept, β, is attributed to P_1 since we consider that[2] $P_1 = k_{reaction} (k_{reaction} + k_{diffusion})^{-1}$. By assigning arbitrary values to P_1 at some chosen temperature we can evaluate other groups of parameters. Thus, since for the recombination process

$$P_t P_{35}^{-1} = \beta_{\lambda 1, t}\beta^{-1}\lambda_{1, 35} = \beta_{\lambda 2, t}\beta^{-1}\lambda_{2, 35}$$

we may write

$$\frac{\beta_{35}}{\beta_t P_{35}} - 1 = \frac{A_d}{A_r} \exp(E_r - E_d)RT \qquad (6)$$

The temperature dependence of β happens to be the same for both reaction systems and all values of

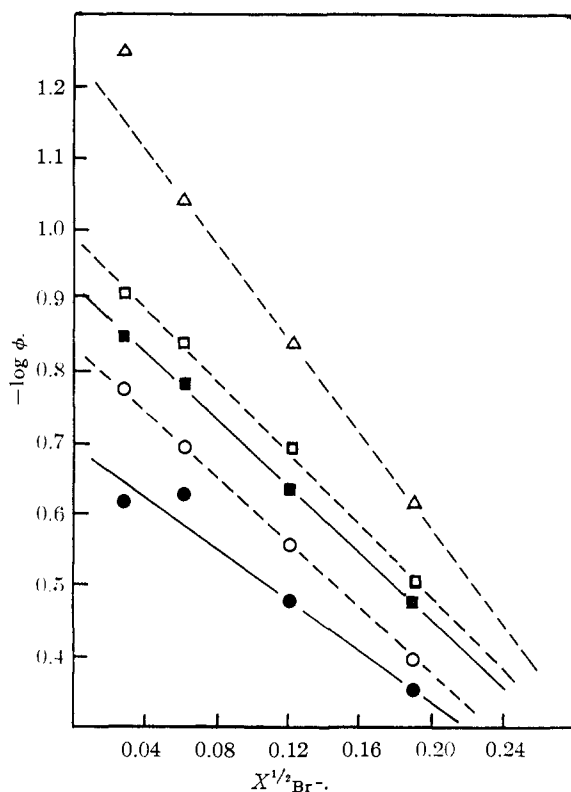(14) R. O. Griffith, A. McKeown and A. G. Winn, Trans. Faraday Soc., 28, 101 (1932).

Fig. 3.—Logarithm of quantum yield for reduction of Br_2 by Mn(II) with square root of mole fraction of Br^-, from the data of Rutenberg and Taube, ref. 4: continuous curves 3650 Å.; broken curves 4360 Å.; circles 35°, squares 19°, triangles 2.5°.

$\beta_t\beta_{35}^{-1}$ at each temperature are combined for considering this effect. For $P_{35} = 0.2$ and 0.4 equation 6 leads to values $E_d - E_r = 2.7$ and 4.0 kcal., respectively. Graphing log $(\beta_{35}\beta_t^{-1}P_{35}^{-1} - 1)$ vs. T^{-1} for each of these trial values of P_{35} leads to equally acceptable linear curves and to a plausible range of values for $E_d - E_r$.

TABLE I

SUMMARY OF RESULTS FOR FIGURES 2 AND 3

| t, °C.	2.5		19		28		35	
λ	4360	3650	4360	3650	4360	3650	4360	3650
				Tribromide				
β			1.585	1.490	1.405	1.335	1.304	1.235
$\beta_t\beta_{35}^{-1}$			1.212	1.207	1.072	1.080	1.000	1.000
μ			4.23	4.35	3.93	3.07	2.90	2.84
$\mu\beta^{-1}$			2.67	2.92	2.80	2.30	2.20	2.30
$\beta_{4360}\beta_{3650}^{-1}$			1.06		1.05		1.06	
				Tribromide				
β	1.240		0.990	0.92			0.840	0.75
$\beta_t\beta_{35}^{-1}$	1.48		1.18	1.23			1.00	1.00
μ	3.08		2.54	2.34			2.34	2.1
$\mu\beta^{-1}$	2.48		2.51	2.54			2.78	2.8
$\beta_{4360}\beta_{3650}^{-1}$			1.07				1.10	

Within experimental error it appears that slope and intercept have the same temperature dependence. From the average value of all such ratios, $\mu\beta^{-1} \cong 2.6$, it follows from equation 1b that $\bar{R}_0 P_2$. $L^{-1} = (\mu/1.78\,\beta)^2 \cong 2.1$.

From equation 1b, $\gamma\rho_0 = 0.174\,P_1\beta^{-1}$; for $P_{1.35} = 0.2$ or 0.4, $\gamma\rho_0 = 0.03$ or 0.06 in triiodide and 0.04 or 0.09 in tribromide. If we remember that these

reduced parameters are expressed in units of collision diameters for the recombination process, $d_{collision} = 0.5(d_{X_2^-} + d_{X^-})$, then the values of L and $\bar{R}_0$ appear to correspond very approximately to the diameter of a molecule of solvent.

The preceding approximations evidently obliterate the smaller numerical effects and a different approach is required to consider the effect of wave length of light absorbed. From equation 1b it would be expected that this effect would alter only ρ_0, neglecting the term in W_0. Within the reliability of the measurements the results in Table I bear out this expectation; that is, by equation 1b the ratio $\beta_{4360}\beta_{3650}^{-1} = \bar{R}_{0,3650}^{-1}\bar{R}_{0,4360}^{-1}$ should be independent of temperature for a given substrate but would be expected to vary with the substrate. Referring to Table I, this appears to be the case.

Durrant, Griffith and McKeown[15] also have measured the photodissociation–recombination of iodine in the presence of iodide and nitrite ions for a variety of conditions. The quantum yield is independent of the concentration of iodine and of light intensity. Since in this reaction system increasing concentrations of iodide ion decrease the quantum yield of iodine reduced, whereas relatively large concentrations of nitrite ion increase the quantum yield, we may postulate the mechanism

$$I_3^- + h\nu \longrightarrow I_2^- + I\cdot$$
$$NO_2^- + I\cdot \longrightarrow NO_2 + I^-$$
$$NO_2^- + I_2^-\cdot \longrightarrow \text{no reaction}$$
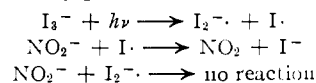
For the case that $(NO_2^-) \gg (I^-)$, but $(I_3^-) \gg (I_2)$, nitrite ion will act simultaneously as the solute inhibiting recombination and as the scavenger for iodine atoms. The effect of nitrite ion can be described adequately by the diffusion equation as $-\log \Phi$ vs. $X_{NO_2^-}^{1/2}$ and in Fig. 4 we compare their results at 4360 Å. and 25° with our measurements described above at 4360 Å and 28°. The similarity of the results justifies the assumed similarity of dissociation–recombination mechanisms.
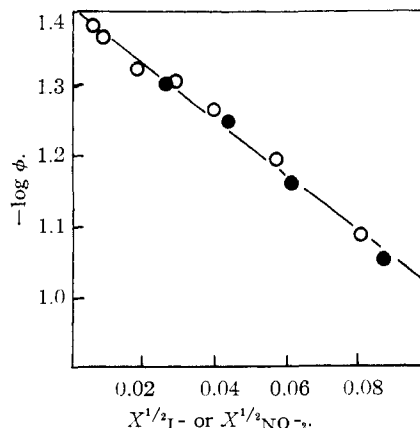

Fig. 4.—Logarithm of quantum yield for reduction of I_2 vs. square root of mole fraction of reagent: this work, I^- at 4360 Å., 25°, solid circles; work of Durrant, et al., ref. 12, NO_2^- at 4360 Å., 28°, open circles.

The thermal reaction between Mn(II) and iodine in the presence of iodide ion at 60° proved to be

(15) G. G. Durrant, R. O. Griffith and A. McKeown, Trans. Faraday Soc., 34, 389(1938).

substantially first order in total iodine, first order in iodide ion and zero order in Mn(II) as appears from the summarized results, Table II. If we postulate a mechanism analogous to reactions 2–5 above it would follow that

$$k_{obs} = k_0(1 - W_\infty)$$

and

$$\log k_{obs} = \log k_0 - \beta + \mu X_{I^-}^{-1/2}$$

where k_{obs} is the first-order rate constant with respect to iodine, k_0 is the "actual" rate of dissociation and $1 - W_\infty$ is the iodide ion dependent probability of non-recombination described by equation

TABLE II

THERMAL REACTION BETWEEN I_3^- AND Mn(II) WITH ADDED I^- AT 60°

Mn(II), $M \times 10^3$	$I_2 + I_3^-$, $M \times 10^3$	I^-, M^a	$k \times 10^4$, min.$^{-1}$	$kM_{I^-}^{-1} \times 10^4$ min.$^{-1}$ mole^{-1} l.
2.3	3.5	0.59	4.4	7.3
2.1	5.8	.40	2.6	6.4
2.1	2.9	.40	2.7	6.8
1.1	3.0	.40	2.6	6.6
1.1	6.1	.40	2.5	6.2
1.1	3.1	.20	1.3	6.7
1.2	6.0	.10	0.77	7.7
1.2	3.0	.10	.79	7.9
0.76	2.8	.049	.75	15

^{a} Stoichiometric concentration.

1b. One actually finds such a linear dependence (not shown) but $\mu_{thermal} = 11$ whereas $\mu_{photo} = 1.4$ by extrapolation to 60°.

An alternative interpretation of these results employs the primary process

$$I_3^- + I^- \longrightarrow I_2^{-\cdot} + I_2^{-\cdot} \qquad (7)$$
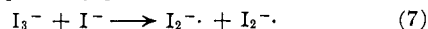
If the reaction of $I_2^{-\cdot}$ with Mn(II) is as efficient as has been postulated for the photochemical reaction, then the steady-state relation

$$\underset{\longrightarrow}{k_7}(I_3^-)(I^-) = \underset{\longleftarrow}{k_7}(I_2^{-\cdot})^2 + k_4(I_2^{-\cdot})(Mn(II))$$

evidently can be simplified by ignoring the term in $(I_2^{-\cdot})^2$ and

$$rate = k_7(I_3^-)(I^-)$$

The test of this rate law appears in the fifth column of Table II. Except that the point at 0.049 M_{I^-} is discordant for each of these treatments, either method furnishes an adequate empirical description of the results. Since we are unable to account for the observed difference between slopes of the photochemical and thermal diffusion functions we prefer mechanism (7).

Acknowledgment.—We are grateful to Dr. R. M. Noyes for helpful criticism, and for an opportunity to read an unpublished manuscript. We greatly appreciate several helpful discussions with Professor J. L. Magee and Dr. L. Monchick.
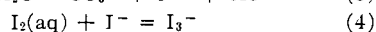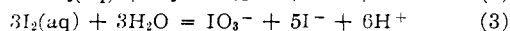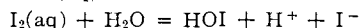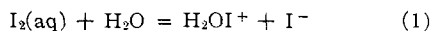
NOTRE DAME, INDIANA

The Formation of Hypoiodous Acid and Hydrated Iodine Cation by the Hydrolysis of Iodine

BY T. L. ALLEN AND R. M. KEEFER

By means of spectrophotometric analyses of aqueous solutions of iodine it has been possible to determine the equilibrium constant for the reaction $I_2(aq) + H_2O(l) = HOI(aq) + H^+(aq) + I^-(aq)$. This constant is 5.40×10^{-13} at 25.0° and 0.49×10^{-13} at 1.6°. It has also been possible to set an upper limit of 1×10^{-10} for the equilibrium constant at 25.0° of the reaction $I_2(aq) + H_2O(l) = H_2OI^+(aq) + I^-(aq)$. The thermodynamic properties of HOI(aq) are calculated.

Aqueous solutions of iodine exhibit absorption maxima in the neighborhood of 288, 352 and 462 $m\mu$.[1,2] The first two of these peaks are attributed to triiodide ion and the longest wave length peak is due to solvated iodine. The triiodide ion in these solutions is a result of the reaction (eq. 4) of iodine with the iodide ion produced by impurities or by hydrolytic reactions of iodine (eq. 1, 2, 3). The rate of production of hypoiodous acid is known to be

$$I_2(aq) + H_2O = H_2OI^+ + I^- \qquad (1)$$
$$I_2(aq) + H_2O = HOI + H^+ + I^- \qquad (2)$$
$$3I_2(aq) + 3H_2O = IO_3^- + 5I^- + 6H^+ \qquad (3)$$
$$I_2(aq) + I^- = I_3^- \qquad (4)$$

very rapid.[3] It has been postulated that the hydrated iodine cation (H_2OI^+) is a precursor[4] of hypoiodous acid. In any case it would be possible to form the hydrated iodine cation by a rapid addi-

tion of hydrogen ion to hypoiodous acid, so that the rate of establishment of the equilibrium represented by eq. 1 must be rapid. Reaction 4 is also quite fast.

Although the equilibrium constant for the formation of iodate ion (eq. 3) is extremely small,[5] the reaction would go far enough to produce appreciable amounts of iodide ion in solutions of $pH > 2$. However, the reaction is slow in acid solutions.[6] From the rate law given by Bell and Gelles,[6] it may be shown that in the presence of the iodide ion formed by reaction 2 the rate of reaction 3 is inversely proportional to the square of the hydrogen ion concentration.

Since equilibria (1), (2) and (4) are established in freshly prepared iodine solutions and equilibrium (3) may be neglected, then, if there is no iodide ion present because of impurities, the concentration of iodide ion produced must be equal to the sum of

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