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

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

and

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

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

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.

An alternative interpretation of these results employs the primary process

$$I_3^- + I^- \longrightarrow I_2^-\cdot + I_2^-\cdot \quad (7)$$

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

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

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

$$\text{rate} = k_7(I_3^-)(I^-)$$

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).

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

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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 mμ.[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

$$I_2(aq) + H_2O = H_2OI^+ + I^- \quad (1)$$

$$I_2(aq) + H_2O = HOI + H^+ + I^- \quad (2)$$

$$3I_2(aq) + 3H_2O = IO_3^- + 5I^- + 6H^+ \quad (3)$$

$$I_2(aq) + I^- = I_3^- \quad (4)$$

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 addition 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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[1] J. J. Custer and S. Natelson, *Anal. Chem.*, **21**, 1005 (1949).

[2] L. I. Katzin, *J. Chem. Phys.*, **21**, 490 (1953).

[3] H. A. Liebhafsky, THIS JOURNAL, **53**, 2074 (1931).

[4] K. J. Morgan, *Quart. Rev.*, **8**, 123 (1954).

[5] W. O. Lundberg, C. S. Vestling and J. E. Ahlberg, THIS JOURNAL, **59**, 264 (1937).

[6] R. P. Bell and E. Gelles, *J. Chem. Soc.*, 2734 (1951).

the concentrations of hypoiodous acid[7] and the hydrated iodine cation

$$(I^-) + (I_3^-) = (H_2OI^+) + (HOI) \qquad (5)$$

By utilizing the equilibrium constants for equations 1, 2 and 4, it is possible to eliminate the terms (H_2OI^+), (HOI) and (I^-) from equation 5 and to rearrange the equation to give equation 6

$$K_1 + \frac{K_2}{(H^+)} = \frac{(I_3^-)^2 y_\pm^2}{K_4(I_2)^2}\left[1 + \frac{1}{K_4(I_2)}\right] \qquad (6)$$

All concentrations are expressed in moles per liter and $y\pm$ is the mean activity coefficient of the ions and is assumed to be the same for all the univalent ions present. The concentration of iodine may be determined from the optical density of the freshly prepared iodine solutions at 462 mμ where the absorption is almost entirely due to solvated iodine. The concentration of triiodide ion may then be determined from the optical density at 288 or 352 mμ after subtracting the absorption due to iodine. It is then possible to evaluate the right side of eq. 6 and plot the values obtained against the reciprocal of the hydrogen ion concentration. The resulting plot should be a straight line whose intercept would be K_1 and whose slope would be K_2.[8]

Experimental

In order to remove any iodide impurities in the iodine, solutions of iodine in carbon tetrachloride were prepared and washed repeatedly with conductivity water. The iodine solutions and conductivity water were placed in glass stoppered flasks, and the flasks were rotated in a thermostat at 25° for several hours. Then the aqueous phases were pipetted off and fresh conductivity water was added. This washing process served to remove both iodide and other water-soluble impurities in the iodine and also to remove iodide formed by reaction of iodine with any traces of reducing agents in the carbon tetrachloride.

The aqueous phase in each flask was then replaced with one of ten buffer solutions which were of the same ionic strength ($\mu = 0.01$), and which ranged in *p*H from 2.04 to 5.67. The buffer solutions were prepared from perchloric acid, sodium perchlorate, sodium acetate and water. In the case of the more acid solutions (*p*H of 2.04 and 3.04) in which the rate of oxidation of iodide ion by oxygen might have been appreciable, the air was displaced by bubbling nitrogen through the solutions. The flasks were covered with aluminum foil to exclude light, shaken vigorously for several minutes, and then rotated in the thermostat for approximately one hour. During this period the iodine distributed between the two phases, and the equilibrium concentration of I_3^- in the aqueous phase, resulting from reactions 1, 2 and 4, was established.

Samples of the aqueous phase were withdrawn by forcing the sample into a pipet with compressed air or nitrogen. The samples were placed in one-cm. ground-stoppered quartz cells, and the optical densities of the solutions were measured with a Beckman type DU spectrophotometer. Optical densities were corrected for light absorption by the cells and buffer solutions.

The cell compartment of the spectrophotometer was equipped with a water jacket through which water from the 25.0° thermostat was circulated. In three experiments after measurement of the optical densities at 25.0°, the cell temperature was reduced to 1.6° by circulating ice-water through the jacket, and the optical densities were determined at that temperature. To prevent condensation of moisture on the cell windows at the lower temperature, the cell compartment was swept out continually with a stream of dry, chilled nitrogen.

It was noted that the concentration of I_3^- increased with time, as evidenced by an increase in the optical densities at 288 and 352 mμ. The rate of increase was very low except in the solutions of $pH > 4.8$. In the less acid solutions the rate of change increased markedly with increasing *p*H. It is probable that the increase in I_3^- concentration was caused by a slow reaction of iodine with traces of reducing agents in the buffer solutions, which in the region of higher *p*H was accompanied by the hydrolysis of iodine to produce iodate (reaction 3). For solutions of $pH > 4.8$, the optical densities were extrapolated to the time of mixing the buffer solution with the iodine-carbon tetrachloride solution.

Hydrogen ion concentrations were calculated from the known concentrations of perchloric acid, acetic acid and acetate ion, and the ionization constant of acetic acid at the temperature of the solution.[9] The activity coefficients of the ions were taken to be the same as the activity coefficients of hydrochloric acid in a solution of 0.01 ionic strength at the appropriate temperature.[9] As a check on the calculated hydrogen ion concentrations, the *p*H of each solution was measured with a Beckman *p*H meter. Calculated and observed values were in good agreement, with an average deviation of 0.02 *p*H unit.

Although the wave lengths of the absorption maxima and the extinction coefficients at these wave lengths for aqueous iodine and I_3^- have been determined by Awtrey and Connick,[10] it was considered desirable to check the values they obtained. Essentially the same procedures were followed, except that one cm. cells were used. In determining the extinction coefficients of iodine, it was necessary that the concentration of I_3^- be made sufficiently small that its light absorption was negligible compared to that of iodine. This was accomplished by using solutions containing appreciable concentrations of H^- and IO_3^-, which removed I^- and I_3^- by the reverse reactions of equations 3 and 4. From the most probable values[5,6] for K_1 and K_3, it may be shown that for the reaction

$$6H^+ + IO_3^- + 2I_2 + 2H_2O = 5H_2OI^+ \qquad (5)$$

the equilibrium constant, K_5, is 6×10^{-8}. For the range of concentrations of I_2, IO_3^- and H^- employed in these solutions, most of the IO_3^- was reduced to H_2OI^+. In calculating the extinction coefficients of I_2, it was necessary to neglect any light absorption by the H_2OI^+, as its extinction coefficients are not known. In order to determine whether or not this procedure was introducing appreciable errors, the initial concentration of IO_3^- was varied over a fourfold range. This resulted in no appreciable change in the calculated extinction coefficients.

The water used in all experiments was redistilled from alkaline permanganate solution. Eastman Spectro Grade carbon tetrachloride was redistilled, and a middle fraction of b.p. range 75.9–76.2° (uncorrected) was used. Other chemicals were of a C.P. or Reagent grade.

Results and Discussion

The wave lengths of the absorption maxima and the molar extinction coefficients at these maxima are tabulated in Table I, along with the results of Awtrey and Connick.[10] The agreement between the two sets of results is well within the probable experimental error.

TABLE I

MOLAR EXTINCTION COEFFICIENTS OF I_3^-(aq) AND I_2(aq)

This work			Awtrey and Connick		
Wave length (mμ)	I_3^-	I_2	Wave length (mμ)	I_3^-	I_2
270	....	121	270	17,200	121
288	40,000	95	287.5	40,000	95
352	26,400	20	353	26,400	18
462	1,030	742	460	975	746

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[7] The ionization constant of HOI is so small (4.5×10^{-13}) that in acid solutions the concentration of OI^- is negligible. See A. Skrabal, *Ber.*, **75B**, 1570 (1942).

[8] Katzin[2] has determined K_1 from spectrophotometric measurements of aqueous iodine solutions in which sufficient acid was present to repress reaction 2. However, he obtained evidence that his values were too large because of iodide impurities.

[9] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 580, 547.

[10] A. D. Awtrey and R. E. Connick, THIS JOURNAL, **73**, 1842 (1951).

From these extinction coefficients and the observed optical densities, the concentrations of I_2 and I_3^- in the buffer solutions were calculated. At the concentrations of I^- present in these solutions, its light absorption is negligible. It was necessary to neglect any light absorption by HOI or H_2OI^+, since their extinction coefficients are not known. The concentration of I_3^- was calculated from observations at each of the two I_3^- absorption peaks. The values thus obtained agreed within the experimental error, indicating that neglect of light absorption by HOI and H_2OI^+ caused no serious error. The best value of I_3^- was taken as the average of the two independent determinations.

The most probable values for K_4 were considered to be those calculated from the equation relating this equilibrium constant and the temperature, which is given in the paper by Davies and Gwynne.[11]

The function $K_1 + K_2/(H^+)$ was then calculated from the experimental results at the various hydrogen ion concentrations. Average values for experiments within the range of $1/(H^+)$ from 1×10^2 to 12×10^3 are shown in Fig. 1, and those at higher values of $1/(H^+)$ are shown in Fig. 2. The accuracy of the experimental points is greater for those experiments shown in Fig. 2. At low values of $1/(H^+)$ (high acidity) reaction (2) is sufficiently repressed that most of the light absorption at the I_3^- absorption peaks is caused by I_2, and against this relatively high I_2 background it is difficult to determine I_3^- with accuracy.

For those experiments shown in Fig. 2, K_1 is negligible compared to $K_2/(H^+)$. Therefore K_2 may be determined by multiplying the value of $K_1 + K_2/(H^+)$ for each experiment in this range by (H^+). This procedure has the merit that the experiments may be equally weighted. The value of K_2 as determined in this fashion is $(5.40 \pm 0.25) \times 10^{-13}$ at 25.0° and $(0.49 \pm 0.03) \times 10^{-13}$ at 1.6°. The slopes of the straight lines in Figs. 1 and 2 were made equal to these values. The intercept of the straight line in Fig. 1 was adjusted to give the closest agreement with the several experimental points. Because of the small size of the intercept (K_1) and the uncertainties in the experimental points it is not possible to determine the intercept with accuracy. However, one may set an upper limit to K_1 of 1×10^{-9} at 25.0°. Since in Fig. 2 this intercept is negligibly small, and since it would be expected to be even smaller at 1.6°, the straight lines were drawn to pass through the origin. It may be seen that the points lie close to the straight lines.

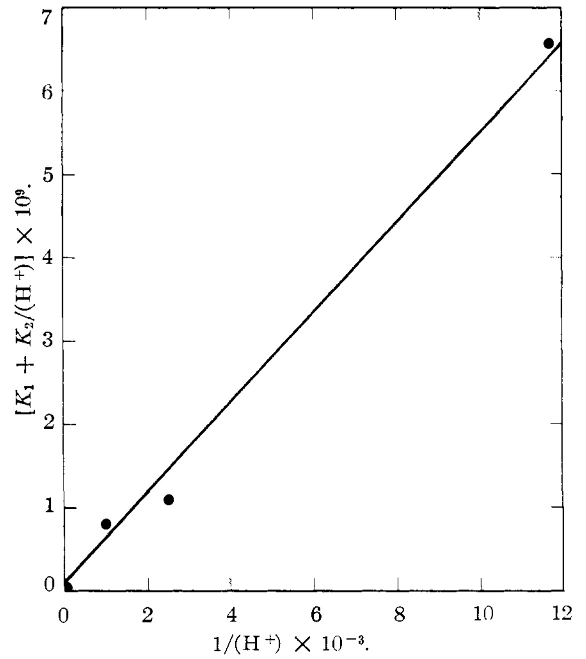

Fig. 1.—The dependence of $K_1 + K_2/(H^+)$ on the reciprocal of the hydrogen ion concentration at high acidity and at 25.0°.

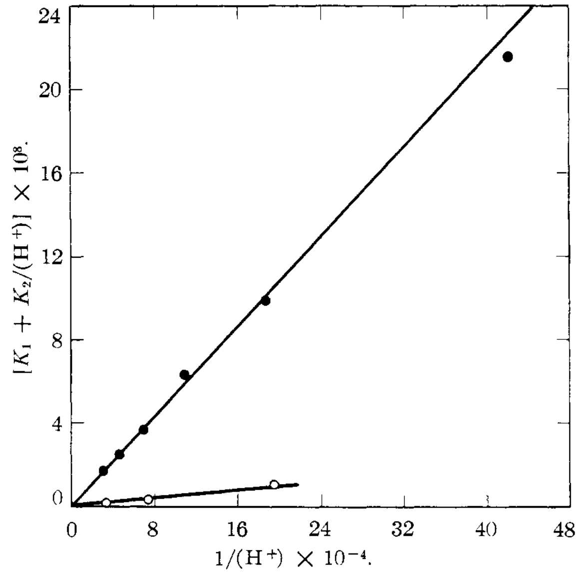

Fig. 2.—The dependence of $K_1 + K_2/(H^+)$ on the reciprocal of the hydrogen ion concentration at low acidity: ●, 25.0°; ○, 1.6°.

In order to determine K_1, solutions of iodine in aqueous perchloric acid of higher acidity were then investigated, using 10-cm. cells for determination of the ultraviolet spectra. Samples were analyzed approximately one-half hour after mixing the iodine–carbon tetrachloride solution and the perchloric acid solution to decrease errors from the slow increase in triiodide concentration mentioned previously. Results are shown in Table II. At these low concentrations of I_3^-, the smaller extinction coefficient of I_2 at 352 mμ makes this wave length more favorable than 288 mμ for determination of I_3^-. Values of (I_3^-) in Table II were accordingly obtained from observations at 352 mμ. The perchloric acid solutions were prepared from either Mallinckrodt A. R. 60% $HClO_4$ (M) or Baker Reagent 60% $HClO_4$ (B), and were either air-saturated or nitrogen-saturated. The presence of oxygen made no difference in the results, at least within the experimental error. This is probably due to the low rate of oxidation of iodide ion by oxygen at these low iodide concentrations. The source of the perchloric acid made an important

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[11] M. Davies and E. Gwynne, THIS JOURNAL, **74**, 2748 (1952).

difference. The 1.0 *M* $HClO_4$ solution prepared from Baker $HClO_4$ had a much lower triiodide concentration than the comparable solution prepared from Mallinckrodt $HClO_4$. This could be caused by a reducing impurity in the solution prepared from Mallinckrodt $HClO_4$, or an oxidizing impurity in the solution prepared from Baker $HClO_4$. Since the 0.1 *M* $HClO_4$ (M) had only about one-tenth as high a value of (I_3^-) as the 1.0 *M* $HClO_4$ (M) it appears that the former explanation is correct. Whether the impurity was present in the original reagent or was introduced in the preparation of the solution was not established. However, the evidence is sufficient to indicate that the triiodide concentration for the first solution of Table II is in error by a large amount.

TABLE II

ANALYSES OF SOLUTIONS OF HIGH ACIDITY

($HClO_4$), mole/l.	(I_2) × 10^3, mole/l.	(I_3^-) × 10^7, mole/l.
1.0 (M)	1.13	4.9
0.1 (M)	1.15	0.5
1.0 (B)	1.09	0.9

Unfortunately the triiodide concentrations for the second and third solutions are too small to be determined with accuracy. The iodine background makes up 95 and 90%, respectively, of the light absorption at 352 mμ. Therefore it may be concluded that K_1 is too small to be determined by this method. It is possible to set an upper limit to K_1 of 1×10^{-10} from these experiments.

Values[12,6,2] previously reported for K_1 at 25° are 1×10^{-8}, 1.2×10^{-11}, and a group of values ranging upwards from 0.52×10^{-8}. The only one of these which is less than the upper limit given above is 1.2×10^{-11}, and it is therefore taken as the most probable value of K_1.

TABLE III

THE EQUILIBRIUM CONSTANT FOR REACTION 2

$K_2 \times 10^{13}$	t, °C.	Method
5.4	25.0	This investigation
0.49	1.6	This investigation
3	25	Conductivity of aq. iodine solns.[a]
0.09	0	Conductivity of aq. iodine solns.[b]
11	25	Kinetic studies[c]
1.5	20	Iodometric titration error.[d] Results probably in error due to neglecting formation of I_3^-
4.6	25	*p*H of iodine solns.[13]

[a] W. C. Bray and E. L. Connolly, THIS JOURNAL, **33**, 1485 (1911). [b] G. Jones and M. L. Hartmann, *ibid.*, **37**, 241 (1915). [c] A. Skrabal, *Z. Elektrochem.*, **17**, 665 (1911). [d] E. Angelescu and V. D. Popescu, *Z. physik. Chem.*, **A156**, 304 (1931).

The value of 5.4×10^{-13} for K_2 obtained in this investigation is in good agreement with the value[13] calculated from the *p*H of aqueous iodine solutions. Reported values of K_2 are summarized in Table III.

The dissociation constant of the cationic acid H_2OI^+, according to the reaction

$$H_2OI^+ = H^+ + HOI$$

is given by the ratio K_2/K_1. At 25.0° this is 4.5×10^{-2}.

From the equilibrium constant at 25.0 and 1.6° the thermodynamic constants of reaction 2 have been calculated assuming that ΔH^0 is temperature independent in the range from 1.6 to 25°.

$$\Delta F^0_{298.16} = +(16.74 \pm 0.03) \text{ kcal./mole}$$
$$\Delta H^0_{298.16} = +(16.7 \pm 0.6) \text{ kcal./mole}$$
$$\Delta S^0_{298.16} = (0 \pm 2) \text{ cal./deg. mole}$$

The standard state for all substances is taken as the hypothetical ideal state of unit molarity. By combining these constants with known thermodynamic properties[14] of other substances which enter into reaction 2 one may obtain the thermodynamic properties of HOI(aq)

$$\Delta F_f{}^0_{298.16} = -23.67 \text{ kcal./mole}$$
$$\Delta H_f{}^0_{298.16} = -33.2 \text{ kcal./mole}$$
$$\Delta S_f{}^0_{298.16} = -32 \text{ cal./deg. mole}$$
$$S^0_{298.16} = 22 \text{ cal./deg. mole}$$

The heat of formation may be compared with the results of Skrabal[15] and Skrabal and Buchta[16] who determined the heat of the reaction

$$I_3^- + OH^- = HOI + 2I^-$$

Combination of their results with known thermodynamic properties of the other substances[14] gives heats of formation for HOI(aq) of −34.7 and −36.3 kcal./mole, respectively.

Acknowledgment.—It is with pleasure that the authors acknowledge the financial assistance of a research grant from the National Science Foundation.

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(12) H. D. Murray, *J. Chem. Soc.*, **127**, 882 (1925).

(13) G. Horiguchi and H. Hagisawa, *Bull. Inst. Phys. Chem. Research (Japan)*, **22**, 661 (1943).

(14) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500 (1952).

(15) A. Skrabal, *Monatsh.*, **33**, 99 (1912).

(16) A. Skrabal and F. Buchta, *ibid.*, **35**, 697 (1914).