THE DISPROPORTIONATION OF HYPOIODOUS ACID

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(Received 15 May 1979; accepted for publication 23 May 1979)

Abstract—The disproportionation of dilute aqueous iodine solutions was studied by a combination of spectrophotometric and potentiometric methods between pH 7 and 10. The rapid hydrolysis of iodine to yield hypoiodous acid is followed by a slow disproportionation to iodate and iodide. The rate expression

 $-\frac{d[\Sigma I_2]}{dt} = (2.5 \pm 1.6) \times 10^2 \text{ s}^{-1} \text{ l} \text{ mole}^{-1} [\text{HOI}]^2 + (1.2 \pm 0.1) \times 10^2 \text{ s}^{-1} \text{ l} \text{ mole}^{-1} [\text{HOI}][\text{OI}^{-1}]$

was found to fit the rate of disproportionation between pH 7 and 14.

INTRODUCTION

Although numerous articles pertaining to iodine hydrolysis have been published in the past 100 yr[1-6], the advent of pressurised-water reactors has rekindled interest[7,8] in aqueous iodine behaviour in very dilute solutions (ca. 10^{-8} moles 1^{-1}). Evidence suggesting the existence of a volatile and reactive form of iodine, possibly HOI, and the observation that organic iodides are formed[7] under fission product release conditions have further stimulated interest in the chemistry of iodine at very low concentrations.

Iodine hydrolysis at 25°C in dilute aqueous solutions between 10^{-5} and 10^{-4} moles l^{-1} and pH 6 and 10 are reported in this study. Concentrations of I₂ and I₃⁻ are determined spectrometrically while the concentration of I⁻ is determined by use of an iodide ion selective electrode. From these concentrations and the total amount of iodine oxidant in the system, the concentration of HOI is calculated. From these data, rate expressions are suggested which explain aqueous HOI behaviour.

EXPERIMENTAL

Spectrophotometric method. Molar absorptivities for I_3^- and I_2 at 353 nm and 460 nm have been determined [9, 10]. Molar absorptivities [9] for I_2 of 18 and 746 moles⁻¹ cm⁻¹ litres at 353 and 460 nm, respectively, were used in the calculations. The molar absorptivities for I_3^- were redetermined and values of 2.58 ± 0.02 and 955 ± 2 moles⁻¹ cm⁻¹ litres at 353 nm and 460 nm, respectively, were used. These values were within 2% of the values reported by previous workers [9, 10]. Based on these values of the molar absorptivities, a path length of 10 cm and the assumption that none of the iodine hydrolysis products have a significant contribution to the absorbance at these wavelengths, the concentrations of I_3^- and I_2 are calculated from,

 $[I_3^-] = 3.88 \times 10^{-6} \, \mathrm{A}^{353} - 9.35 \times 10^{-8} \, \mathrm{A}^{460} \tag{1}$

$$[I_2] = 1.34 \times 10^{-4} \,\text{A}^{460} - 1.28 [I_3^{-1}] \tag{2}$$

where A^{353} and A^{460} represent the measured absorbances at the specified wavelength.

Buffer solutions of 0.15 moles l^{-1} ionic strength were prepared by combining appropriate amounts of CO₂-free NaOH with NaH₂PO₄ for the pH 6, 7 and 8 studies, with boric acid for the pH 9 study and with NaHCO₃ for the pH 10 study in distilled water. All chemicals were of reagent grade quality.

Prior to each experimental run a base line was established between 325 nm and 750 nm with the appropriate buffer in 10 cm quartz cells. A known amount of I2 dissolved in 0.5 ml of diethyl ether was injected rapidly into 100 ml of N2-saturated buffer which was pre-equilibrated at 25°C and vigorously mixed. The test solution was transferred to the spectrophotometer cell and positioned within the sample compartment of the spectrophotometer within 60 sec of mixing. The temperature of the cell compartment was maintained at 25±0.5°C by circulation of thermostatted water through the surrounding jacket. The base line was zeroed at 750 nm, a wavelength at which neither I2 nor I_3^- absorb, and spectral scans at a rate of 10 nm sec⁻¹ were made at selected times from 2 min to 4 days after introduction of the I2. No correction was made for the 11 sec time interval separating the two wavelength measurements. The concentrations of I2 and I_3^- were calculated by use of eqns (1) and (2).

Ion selective electrode measurements. An Orion iodide ion selective electrode (Model 94-53) and mercury-mercurous sulphate reference electrode were used. Contamination of the test solution was avoided by use of a flowing bridge. Approximately 50 ml hr⁻¹ of the appropriate buffer passed through the bridge with 0.3 ml hr⁻¹ passing through the ultra-fine frits. The reference electrode was held at ambient temperature $\pm 0.4^{\circ}$ C within a styrofoam box during experimental runs while the test solution was maintained at 25.0 ± 0.2°C by use of a water bath. The potential of the cell was recorded by means of a Metrohm Model E 436 Potentiograph.

The potential of the cell is related to the iodide concentration by,

$$E = C + B \log_{10} [I^{-}]$$
(3)

where C is a constant dependent upon the electrode system and B is the Nernst constant. Least squares treatment of calibration data yielded values for B of $-59.2 \pm 1.5 \text{ mV}$ in excellent agreement with the theoretical slope of the Nernst eqn and for C of $-780 \pm 10 \text{ mV}$. No problem was encountered with drift of the

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potential between pH of 6 and 8 although at higher pH the drift approached 4 mV hr^{-1} . Both the response of the electrode and the constant, C, in eqn (3) were affected by prolonged exposure to the buffer solutions. This appeared to be due to a deposit formed on the sensing membrane of the ion selective electrode. Performance of the electrode was restored by polishing the membrane with glass filter paper.

Prior to each experimental run the iodide ion selective electrode was immersed in 200 ml of N₂-saturated buffer for approximately 90 min. The run was initiated by injection below the surface of the rapidly stirred buffer solution, of a known amount of I₂ dissolved in 1 ml of diethyl ether. The potential was recorded for up to 4 hr after injection of the I₂. A calibration was performed by injection of at least 6 potassium iodide standards which was sufficient to swamp the effect of the iodide produced from the hydrolysis but would not significantly alter the ionic strength of the solution. The potential was monitored for 60 min after the calibration to check for drift. If drifting of the potential occurred, the rate of drift was assumed to be constant and the measured potentials corrected by interpolation. The iodide concentrations were calculated using eqn (3).

DISCUSSION

When iodine is introduced into an aqueous solution, a number of rapid reactions occur. The hydrolysis of I_2 to form HOI, as shown in eqn (4), and the formation of I_3^- , as shown in eqn (5), are both diffusion controlled reactions[11]. These reactions are followed by a slower disproportionation of HOI to form IO_3^- and I^- .

$$I_2 + H_2O = HOI + I^- + H^+$$
 (4)

$$I_2 + I^- = I_3^-$$
 (5)

$$3HOI = IO_3^- + 2I^- + 3H^+$$
(6)

The over-all reaction for the disproportionation is represented by:

$$3I_2 + 3H_2O = IO_3^- + 5I^- + 6H^+$$
 (7)

Extrapolation to zero time of the ratio of iodide ion to the total iodine concentration introduced to the system yielded values of 0.21, 0.34, 0.60, 0.69 and 0.83 at pH values of 6, 7, 8, 9 and 10, respectively. The initial fraction of iodide, f_{1-} , was estimated from,

$$K_4 = \frac{(f_{\rm I})^2 (\Sigma I_2)_0 a_{\rm H^+}}{(1 - f_{\rm I^-})} \frac{\gamma_{\rm HOI} \gamma_{\rm I^-}}{\gamma_{\rm I_2}}$$
(8)

where $(\Sigma I_2)_0$ was the concentration of iodine introduced to the system, a_{H^+} was the hydrogen ion activity and γ_{HOI} , γ_{I_2} and γ_{I^+} were the activity coefficients of HOI, I_2 and I^- respectively.

Equation (8) ignores the formation of triiodide ion, and the dissociation of hypoidous acid,

$$HOI=H^+ + OI^-$$
 (9)

Inclusion of these two side reactions necessitates an iterative calculation for the fraction of iodide that is formed by the hydrolysis of iodine. Equilibrium constants, $K_4 = 5.4 \times 10^{-13}$ for the hydrolysis[10] $K_5 = 768$ for the triiodide formation[12] and $K_9 = 2.0 \times 10^{-11}$ for the dissociation[13] were used.

The activity coefficients of hypoiodous acid and iodine were assumed to be unity and the activity of iodide ion to be given by [14],

$$-\log \gamma_{\pm} = \frac{0.5 \,\mu^{1/2}}{1 \pm 0.5 \,\mu^{1/2}} \tag{10}$$

The initial fraction of iodide to the total amount of iodine that was introduced to the system was calculated to be 0.13, 0.26, 0.59, 0.71 and 0.99 for pH values from 6 to 10 inclusive, which is in good agreement with the extrapolated data.

The increase in iodide ion concentration showed in Fig. 1 is indicative of disproportionation of the hypoiodous acid as represented by eqn (4) and the over-all reaction for the disproportionation of iodine to iodate may be represented by eqn (7).

The latter equation predicts a ratio of iodide to initial iodine for the reaction going to completion of 1.67. Using the equilibrium constant [15] for the reaction represented by eqn (10) of 6.3×10^{-48} , the theoretical conversion of iodine to iodate is greater than 99.9% at pH values greater than 8. The experimental ratio of iodide to initial iodine approaches although it does not reach 1.67 at the pH values for these experiments. Equilibrium was not attained during the period of observation for the experiments described here. Thus, 25% of injected iodine remained after 4 days at a pH of 7, 1% remained after 14 hr at a pH of 8 and 0.1% remained after 2 hr at a pH of 9. At a pH of 10, the ratio of iodide to initial iodine approached but did not reach the theoretical limit of 1.67; however, the potential was subject to drift beyond a 2 hr period at this pH. Previous investigators have also reported that long periods are required to reach equilibrium. Luther and Sammet[16] have reported that 49 days are necessary at a pH of 6.2, while Sugawara and Terada[17] have reported that iodate was still being produced in sea water after 25 days.

The extent of the disproportionation was determined by the difference between the amount of iodine that was introduced to the system and the concentration of I_2 , I_3^- , HOI and OI⁻ present at any given time as the hydrolysis of I_2 to HOI and OI⁻ was incomplete at the pH's used in this study. Both the I_2 and the I_3^- concentrations were measured directly. The HOI and the OI⁻ concentrations were calculated from,



Fig. 1. Ratio of iodide to total initial iodine as a function of time. Temperature 25.0°C, Ionic strength 0.15 moles litre⁻¹ at pH of 6 ∇ , 7 \diamond , 8 \Box , 9 \triangle and 10 \bigcirc .

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$$[HOI] = K_4[I_2]/[I_1]a_{H^+}$$
(11)

$$[OI^{-}] = K_9[HOI]/a_{H^+}$$
 (12)

The rate of disproportionation of the mixture was found to agree with,

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$$-\frac{\mathrm{d}[\Sigma I_2]}{\mathrm{d}t} = k'[\Sigma I_2]^2 \tag{13}$$

where

$$[\Sigma I_2] = [I_2] + [I_3^-] + [HOI] + [OI^-].$$
(14)

The observed rate constant, k' is the product of the rate constant and the square of the fraction of the reactive component in the mixture. A plot of the reciprocal of the sum of the I₂, I₃⁻, HOI and OI⁻ concentrations, (Σ I₂), as a function of time at pH of 9 was very nearly linear as shown in Fig. 2. Similar plots for pH of 7 and 8 exhibited curvature. These plots were not linear as the fraction of HOI and OI⁻ in the reaction mixture was changing due to the increasing I⁻ concentration as the disproportionation proceeded. A kinetic treatment of the data must take into account that an equilibrium mixture of I₂, I₃⁻, HOI and OI⁻ was being converted into IO₃⁻. Since the correlation was very nearly linear at a pH of 9, the reactive component must be HOI. Thus the rate expression becomes,

$$-\frac{\mathrm{d}[\Sigma I_2]}{\mathrm{d}t} = k \left\{ \frac{1}{1 + \frac{[I^-]a_{\mathrm{H}^+}}{K_4} + \frac{[I^-]^2 a_{\mathrm{H}^+} K_5}{K_4} + \frac{K_9}{a_{\mathrm{H}^+}}} \right\}^2 [\Sigma I_2]^2$$
(15)

where K_4 , K_5 and K_9 are the equilibrium constants for the reactions represented by the corresponding equations.

The rate constant was estimated from the slope of the plot of $[\Sigma I_2]^{-1}$ vs time coupled with the fraction of HOI at that time. The rate constant was also estimated from a numerical integration of

$$\int_{1 \ge I_2 I_1}^{1 \ge I_2 I_2} \frac{d[\ge I_2]}{\left\{1 + \frac{[I^-]a_{H^+}}{K_4} + \frac{[I^-]^2 a_{H^+} K_5}{K_4} + \frac{K_9}{a_{H^+}}\right\}^2 [\ge I_2]^2} = k(t_2 - t_1) \quad (16)$$

which utilised all of the data for the run rather than the estimation of the slope of the curve at a particular point in the course of the reaction and in addition, corrected for the changing HOI concentration. Plots of this correlation were linear at each of the pH values studied. Comparison of these estimations of the rate constant are shown in Table 1.

At pH of 6 insufficient data were obtained during the approach to the steady state condition to allow the rate constant to be estimated. At pH of 10 only data from the ion selective electrode were obtained as the spectrophotometric measurements were not sufficiently sensitive to permit the estimation of I_2 and I_3^- concentrations. The rapid increase in the I⁻ concentration as shown in Fig. 1 is indicative of a rapid disproportionation to IO_3^- and I⁻. At pH of 10 the disproportionation is very nearly complete. An estimation of the extent of the disproportionation as a function of time was made by the use of a set of simultaneous equations based on a total oxidant



Fig. 2. Reciprocal of sum of iodine, triiodide, hypoiodous acid and hypoiodite concentrations as a function of time. Temperature 25.0°C, ionic strength 0.15 moles litre⁻¹ and pH of 9.0.

balance, a total iodine atom balance and the iodide ion concentration. Such an estimation must be used with caution. When the treatment was applied to the sets of data where both spectrophotometric and potentiometric data are available, the estimates of the rate constants from the potentiometric data are approximately 40% of the results from the combined data. Variation of the values of the hydrolysis constant of iodine, or the total iodine concentration did not improve the comparison of the results for pH of 10 are of interest for comparison with the results for pH of 7–9 as shown in Table 1.

These results are consistent with the disproportionation of iodine solutions between pH values of 7 and 10 occurring via HOI as the reactive intermediate as proposed in eqn (13). Extrapolation of this rate expression to higher pH's, such as are the conditions reported by earlier workers, would predict that the observed rate constant would decrease as the square of the hydrogen ion concentration. The predicted rate from this extrapolation would only contribute approximately 1% of the observed rate of the disproportionation as reported by Skrabal and Hohlbaum[3] or as calculated from the data reported by Hashmi [5]. This suggests that at higher pH the rate determining term involves both hypoiodous acid and hypoiodite ion since the decrease in the observed rate constant was directly proportional to the

Table 1. Rate constant for disproportation at 25.0°C and 0.15 moles litre⁻¹ ionic strength

	Rate constant of disproportionation (1 mole ⁻¹ sec ⁻¹)	
рН	From slope of $[\Sigma I_2]^{-1}$ time plot	From numerical integration eqn (16)
7	0.9×10^{2}	1.0×10^{2}
8	3.5×10^{2}	3.0×10^{2}
9	3.3×10^{2}	4.5×10^{2}
10	$1.2 \times 10^2 a$	$1.4 \times 10^2 a$

a Only Ion selective electrode data used at pH 10.



Fig. 3. Logarithm of observed disproportionation rate constant as a function of pH at 25.0°C. -- pH dependence of f_{HOI_2} , f_{OI_2} ; ---- pH dependence of f_{HOI}^2 ; Predicted rate according to eqn (17);
Calculated from data of Li and White (Ref. 2); O Calculated from data of Skrabal (cited in Ref. 2); \triangle This work; determined from slope of reciprocal [ΣI_2] vs time curve.

hydrogen ion concentration. Although Li and White[2] argued against the significance of the term, $k'[OI^-]^2/[OH^-]$, reported by Skrabal and Hohlbaum[3], the calculation of the data of Hashmi between pH of 13 and 14 are in excellent agreement with a reciprocal OHdependence as shown in Fig. 3.

A combination of the two terms to yield the rate expression,

$$\frac{\mathrm{d}[\Sigma \mathrm{I}_2]}{\mathrm{d}t} = k_1(\mathrm{HOI})^2 + k_2(\mathrm{HOI})(\mathrm{OI}^-)$$

gave an excellent fit of the reported disproportionation data between pH of 7 and 14 where k_1 as determined in this study, has the value of $(2.5 \pm 1.6) \times 10^2 \text{ s}^{-1} \text{ l mole}^{-1}$, and k_2 as calculated from the data of Hashmi has the value $(1.2 \pm 0.1) \times 10^2 \text{ s}^{-1} \text{ l mole}^{-1}$.

Acknowledgements-A fellowship from the Associated Western Universities and financial support by the South African Council for Scientific and Industrial Research is greatefully acknowledged (RAH).

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