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Temperature Dependence of the Equilibrium Constant for Iodine Hydrolysis at Temperatures between 25 and 120 °C

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The equilibrium constant for iodine hydrolysis at elevated temperatures has been investigated using absorption spectroscopy and a simulation computer program. The temperature dependence of the aqueous I_2 maximum extinction coefficient for visible light (at 460 nm) was first evaluated in a preliminary experiment using saturated I_2 solution. The time dependence of I_2 concentrations in dilute solution has subsequently been measured using the temperature-dependent extinction coefficient. The results were analysed by the simulation program, in which 11 normally accepted reactions were considered, and the equilibrium constant, K, was estimated. It was concluded that the K value at temperatures ranging between 25 and 120 °C may be expressed by

$$\log K(T) = 13880/T - 0.2445T + 308.4 \log T - 749.1$$

where the units of K and T are $mol^2\ dm^{-6}$ and K, respectively.

It is possible for iodine to be released from defective fuel rods into the surrounding water, or produced from released iodide by radiolytic oxidation under fault conditions in light water reactors. Estimation of the quantity of volatile radioactive iodine formed under such circumstances is important in the assessment of the safety of the reactors with respect to radiological consequences of fault conditions. Computer simulation of iodine chemistry is a useful method for estimating iodine speciation and it has proved to be reasonably successful.[1,2] Simulation predictions of the release of volatile iodine under reactor fault conditions have been shown to be very sensitive to the equilibrium constant for iodine (I_2) hydrolysis.[2] Accurate values of the constant, however, are not known at elevated temperatures.

Molecular iodine, I_2, is rapidly hydrolysed in dilute solution according to

$$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+. \tag{1}$$

This equilibrium is strongly temperature dependent and its constant has been measured only at temperatures below 40 °C.[3] This is because the hydrolysis is followed by the disproportionation reactions given below which are significant, and it is difficult to determine the equilibrium constant separately by experiment:

$$HOI + HOI \rightleftharpoons IO_2^- + I^- + 2H^+ \tag{2}$$

$$HOI + IO_2^- \rightleftharpoons IO_3^- + I^- + H^+. \tag{3}$$

Therefore, the constant above 40 °C has been calculated by extrapolation using thermodynamic data and there are discrepancies in the calculated values.[3–6] For instance, the constant at 100 °C as reported by Turner[3] and by Palmer *et al.*[4] is 4.6×10^{-11} and 2.5×10^{-10} $mol^2\ dm^{-6}$, respectively.

This paper reports work on the experimental determination of the equilibrium constant for I_2 hydrolysis over the temperature range 35–120 °C by comparing the results between experiments and computer simulations. The temperature dependence of the I_2 extinction coefficient for visible light (at 460 nm) was first investigated in a preliminary experiment to measure the I_2 concentration by absorption spectroscopy. The time dependence of the concentration of I_2 in dilute solution was subsequently measured at elevated temperatures using the temperature-dependent extinction coefficient. A computer program was also developed by considering 11 reactions, including reactions (1)–(3), to simulate the I_2 concentration change at high temperatures. The equilibrium constant of the I_2 hydrolysis was then determined for individual temperatures by comparing the experimental and simulation results.

Experimental

The equilibrium of reaction (1) is rapidly established on dissolving I_2. The I_2 concentration decreases with time upon heating because the equilibrium constant increases with temperature and disproportionation also occurs on a longer timescale. The concentration of I_2 at elevated temperatures was measured by absorption spectroscopy. Fig. 1 shows the spectrometer schematically. Light from a monochromator was divided into two beams, reference and sample, and modulated with different chopping frequencies, typically 110 and 270 Hz. These beams were detected by use of a lock-in (phased-locked) amplifier (ORTHOLOC SC-9505), which can measure two different signals simultaneously.[7] The absorbance of the sample was then calculated by a ratiometer. The system allowed measurements to be made at elevated temperatures not possible in commercial spectrometer systems. The accuracy of the I_2 analysis was 2×10^{-7} mol dm^{-3} in this system.

The I_2 concentration in the solution could be reduced by volatilization at high temperatures. In order to prevent significant losses of I_2, experiments were performed using a pressure-resistant quartz cell with an airtight valve and the ratio of gas and liquid volumes in the cell was kept below 5%. Considering the volume ratio and partition coefficient of I_2 between gaseous and liquid phases (*ca.* 10 at 100 °C), the loss of I_2 concentration in the sample solution was estimated to be at most 0.5%.

Preliminary experiments were performed to measure the temperature dependence of the extinction coefficient of I_2 in aqueous solution. The relationship between absorbance, A, and I_2 concentration, C, is expressed by:

$$A = \varepsilon C x \tag{I}$$

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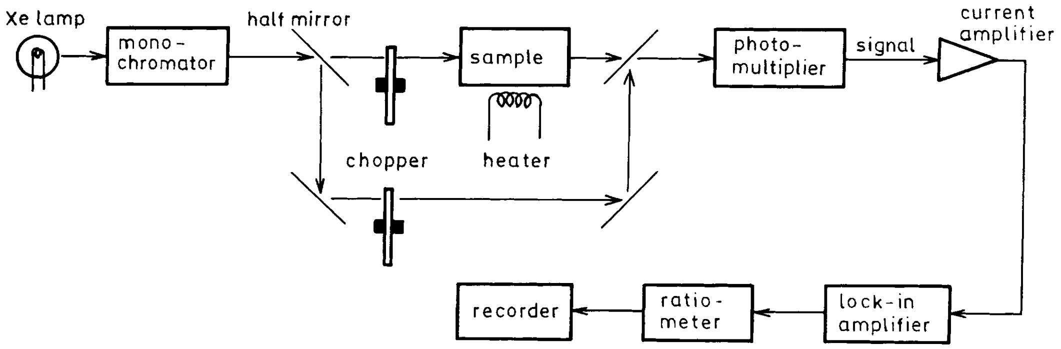

Fig. 1. Schematic diagram of spectrometer.

where ε is the I_2 extinction coefficient and x the optical path-length of the sample cell.[8] ε has its maximum value at 460 nm but only the value at ambient temperature has been reported previously.[9] Therefore, the ε value of I_2 at high temperatures was measured first. Saturated I_2 solution (1.1×10^{-3} mol dm^{-3} at 25 °C) was poured into a 1 cm sample cell and heated to 110 °C. The absorbance of the sample was measured using the spectrometer described to estimate the extinction coefficient for individual temperatures. Saturated I_2 solution was used in this experiment to minimize the I_2 hydrolysis and the small effect of hydrolysis was corrected for by the calculation described in the Results and Discussion section.

Fig. 2 shows a schematic view of the sample cell used in this study to measure I_2 concentration change in dilute solution at elevated temperatures. Boric acid solution (0.01–0.02 mol dm^{-3}) was made up using triply distilled water. About 100 cm^3 of the solution was poured into the vessel, which had a 7 cm optical path-length and 110 cm^3 volume. The solution was stirred and heated to the desired temperature between 35 and 120 °C. Subsequently, 0.4–6.0 cm^3 of saturated I_2 solution was injected into the boric acid solution through the septum and valve shown in fig. 2, to give an aqueous I_2 solution with a concentration of 4–60 μmol dm^{-3}. Partial hydrolysis of the I_2 to form I^- and HOI as described in reaction (1) occurred very quickly before the first measurement, and the absorbance was measured every 5 min to follow the course of the disproportionation of HOI at the chosen temperature.

As described above, the samples were made up in boric acid solution. This was done in order to hold the pH constant against the tendency to change caused by the dissolution of CO_2 from the air during sample preparation, and by the effect of the equilibrium of reaction (1) itself. An accurately known value of H^+ concentration or of pH is essential in determining the equilibrium constant of I_2 hydrolysis.

Simulation Program

A simulation program for iodine hydrolysis was developed to estimate the equilibrium constant at elevated temperatures by comparing experimental and simulated results. The simulation was done with the FACSIMILE/CHECKMAT program,[10] which requires as input information the reaction scheme with rate constants and equilibrium constants of the species involved. The program constructs a series of simultaneous differential equations for the concentration of each species and solves them as a function of time. As output information the program can provide these concentrations at any required time. The program also has a facility called 'VARY' to obtain 'best-fit' values for designated parameters from measured concentrations at given times.

Table 1 summarizes the 11 equilibrium reactions considered in this simulation program. The first nine are normally accepted reactions in I_2/I^- solutions.[1] Volatilization of I_2 and HOI species were also considered in the last two reactions, but these had a negligible influence on the calculated result. This was because the reactions proceeded in a closed vessel and the gas space was much smaller than the liquid volume (gas/liquid = 3.5 vol%) in this study.

The equilibrium constants and rate constants for reactions (3)–(11) were taken from recent publications as shown in table 1. However, the values for reactions (1) and (2) were examined more carefully in the following way, because these are very important reactions in dilute I_2/I^- solutions at high

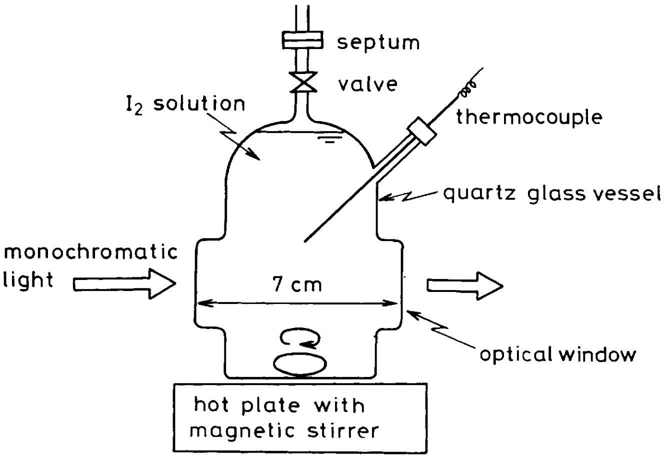

Fig. 2. Schematic view of sample cell.

Table 1. Reactions considered in this simulation program

no.	reaction	ref. equil. const.	ref. rate const.
(1)	$I_2 + H_2O \rightleftharpoons HOI + I^- + H^+$	this study	11, 12
(2)	$2HOI \rightleftharpoons IO_2^- + I^- + 2H^+$	1	this study
(3)	$HOI + IO_2^- \rightleftharpoons IO_3^- + I^- + H^+$	4	1
(4)	$I_2 + I^- \rightleftharpoons I_3^-$	4	14
(5)	$HOI \rightleftharpoons IO^- + H^+$	4	15
(6)	$H_2O \rightleftharpoons H^+ + OH^-$	16	16
(7)	$H_3BO_3 + OH^- \rightleftharpoons H_4BO_4^-$	17	[a]
(8)	$2H_3BO_3 + OH^- \rightleftharpoons H_7B_2O_7^-$	17	[a]
(9)	$3H_3BO_3 + OH^- \rightleftharpoons H_{10}B_3O_{10}^-$	17	[a]
(10)	$I_2\ (g) \rightleftharpoons I_2\ (l)$	18	19
(11)	$HOI\ (g) \rightleftharpoons HOI\ (l)$	18	19

[a] The reaction rate constant was set at 1×10^7 mol dm^{-3}.

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temperatures.[2] The equilibrium constant for reaction (1), K_1, is not known accurately above 40 °C, as stated in the introduction. Therefore, the value was determined by a 'best-fit' method comparing the experimental and simulation results. The forward reaction rate constant for reaction (1) was set at 3 s^{-1}, because the reaction has been found to reach equilibrium within 1 s under most conditions of pH and temperature[11,12] and the reverse reaction rate constant was set equal to k_1/K_1. It is known that HOI decays slowly by second-order kinetics as in reaction (2), and the forward rate constant depends on many factors, such as pH, temperature and boric acid concentration.[13] Therefore, its value was also determined by a best-fit method for the individual experimental conditions. The boric acid reactions (7)–(9) which determine the pH in table 1 reach equilibrium very quickly and their forward constants were set at 1×10^7 dm^3 mol^{-1} s^{-1}, 1×10^7 dm^6 mol^{-2} s^{-1} and 1×10^7 dm^9 mol^{-6} s^{-1} in this program, regardless of temperature; the reverse rate constants were obtained by dividing each forward rate constant by the known[17] equilibrium constant.

Results and Discussion

Effect of Temperature on the Extinction Coefficient

Saturated I_2 solution (1.1×10^{-3} mol dm^{-3} at 25 °C) was heated to 110 °C in a 1 cm sample cell, to estimate the temperature dependence of the I_2 extinction coefficient. The broken line in fig. 3 shows the absorbance changes at 460 nm as a function of temperature. It was apparent that the absorbance decreased with temperature. Absorbance, A, changes with extinction coefficient ε, I_2 concentration, C, and optical path-length, x, as eqn (I). In this experiment, not only ε but also C varied with temperature due to the following two reasons. (i) The solution expanded upon being heated and the C value decreased. This effect was corrected for by using the density of water at high temperatures. (ii) The I_2 was partially hydrolysed at elevated temperatures according to reaction (1) and the C value decreased, this effect in the concentrated I_2 solution being much less than in the dilute one.[1] This effect was corrected for by an iteration method. That is, a test C value was first calculated at each temperature by use of an equilibrium constant, K, for reaction (1) which had been obtained by extrapolation.[3] ε was then evaluated by substituting the test C and observed A values into eqn (I). As described in the next section, K was subsequently estimated using the ε value. C was again calculated using the new K value. Replacing the initial test C by the new C, the same estimation was repeated until the value of C converged. It was determined that C (1.1×10^{-3} mol dm^{-3} at 25 °C) decreased by 5 and 4%, respectively, at 100 °C owing to the above two factors.

The extinction coefficient $\varepsilon(T)$ from 25 to 110 °C was estimated using the corrected C value and published extinction coefficient at ambient temperature (760 dm^3 mol^{-1} cm^{-1}).[9] The solid line in fig. 3 shows the result. A linear relationship existed between ε and T, and the ε value could be expressed by

$$\varepsilon(T) = 1000 - 0.81T \qquad \text{(II)}$$

where the units of ε and T are dm^3 mol^{-1} cm^{-1} and K, respectively.

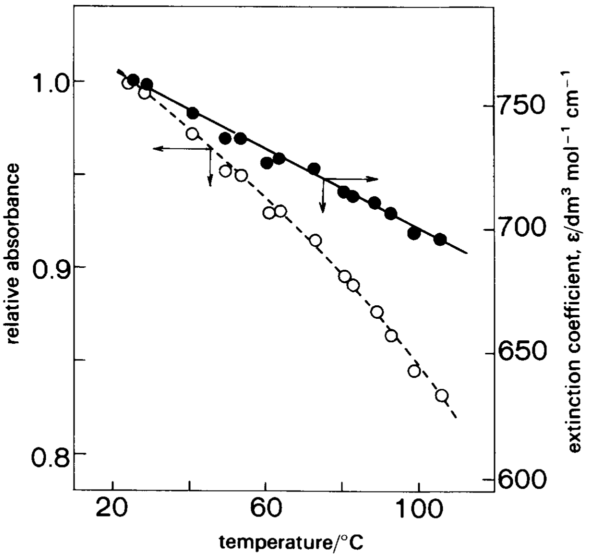

Fig. 3. Temperature dependence of I_2 extinction coefficient, ε, and relative absorbance. Total iodine as $I_2 = 1.1 \times 10^{-3}$ mol dm^{-3}; path-length = 1.0 cm; wavelength = 460 nm.

Effect of Temperature on the Equilibrium Constant

The time dependence of the I_2 concentration at the chosen temperature was measured for times between 5 and 60 min after mixing using dilute solution. Fig. 4 shows experimental and calculated results. The concentration dropped rapidly due to reactions (1) and (4)–(9) in table 1, followed by a very much slower fall due to the reactions (2) and (3). The broken lines in fig. 4 show the calculated results by the 'best-fit' method using a statistically organised set of comparisons in the 'VARY' facility of the simulation program.[10] In the simulation, the equilibrium constant of reaction (1) and rate constant of reaction (2) could be determined by the initial fast drop and the subsequent slower decrease of the I_2 concentration, respectively. Table 2 summarizes the equilibrium and rate constants obtained by this technique, together with the experimental conditions.

Data for the equilibrium constant of reaction (1) are shown in fig. 5 together with the data summarized in ref. (6). The

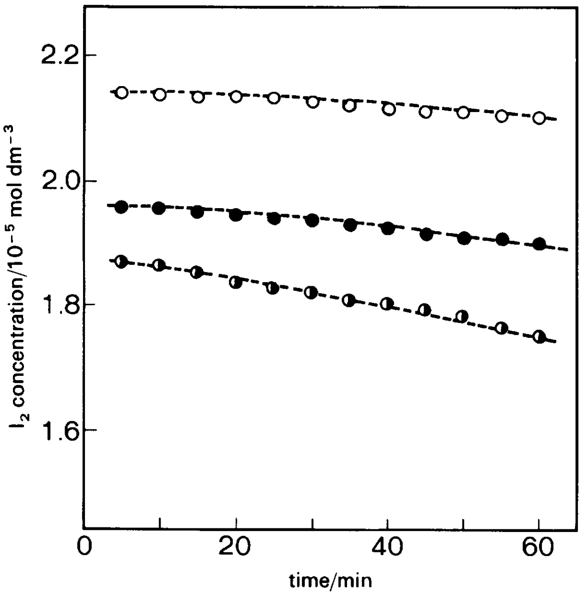

Fig. 4. Time dependence of I_2 concentration in dilute solution at elevated temperatures. Total iodine as $I_2 = 3.0 \times 10^{-5}$ mol dm^{-3}; boric acid = 1.0×10^{-2} mol dm^{-3}. ○, T = 71 °C, $K_1 = 3.2 \times 10^{-11}$ mol^2 dm^{-6}, R_2 = 43 dm^3 mol^{-1} s^{-1}; ●, T = 86 °C, $K_1 = 5.8 \times 10^{-11}$ mol^2 dm^{-6}, R_2 = 47 dm^3 mol^{-1} s^{-1}; ◑, T = 95 °C, $K_1 = 7.8 \times 10^{-11}$ mol^2 dm^{-6}, R_2 = 63 dm^3 mol^{-1} s^{-1}. (---) Calculated.

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Table 2. Summary of experimental results

	experimental conditions			results	
no.	temp/°C	total iodine as I_2/mol^2 dm^{-6}	boric acid /mol dm^{-3}	equil. const. of reaction (1)/mol dm^{-3}	rate const. of reaction (2)/dm^3 mol^{-1} s^{-1}
1	35	4.0×10^{-6}	1.0×10^{-2}	1.4×10^{-12}	ND[a]
2	45			3.3×10^{-12}	
3	53			6.5×10^{-12}	
4	58			1.4×10^{-11}	
5	65			2.2×10^{-11}	
6	40	1.0×10^{-5}	2.0×10^{-2}	1.9×10^{-12}	ND[a]
7	60			1.2×10^{-11}	
8	80			3.9×10^{-11}	
9	40	1.0×10^{-5}	1.0×10^{-2}	1.8×10^{-12}	ND[a]
10	70			2.0×10^{-11}	
11	75			3.1×10^{-11}	
12	75			3.5×10^{-11}	
13	71	3.0×10^{-5}	1.0×10^{-2}	3.2×10^{-11}	43
14	86			5.8×10^{-11}	47
15	95			7.8×10^{-11}	63
16	99			9.8×10^{-11}	83
17	108	6.0×10^{-5}	1.0×10^{-2}	1.4×10^{-10}	98
18	115			1.6×10^{-10}	>100

[a] ND = not determined.

following results were derived. (i) The constant below 40 °C agreed with the result by Eguchi *et al.*[20] (ii) Almost the same constant was obtained at the same temperature, independent of iodine and boric acid concentrations. (iii) The value above 40 °C has previously been calculated by extrapolation based on thermodynamic data. This has led to some discrepancy in the reported values, as is shown by lines A–D in fig. 5. It can be seen that the present data deviated from the extrapolated evaluation by Palmer *et al.*[4] (line D) at temperatures above 80 °C and fell between the prediction of Turner[3] (line A) and the upper values suggested by Lemire *et al.*[5] (line C). (iv) Considering the experimental data obtained in this study and those of Eguchi *et al.*,[20] the equilibrium constant $K(T)$ at temperatures ranging between 25 and 120 °C can be expressed by

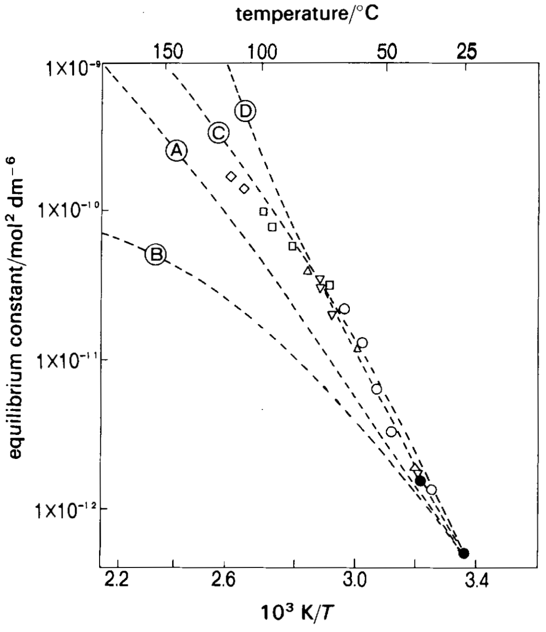

Fig. 5. Temperature dependence of the equilibrium constant for iodine hydrolysis. Summarized in ref. (6): A, calculated[3]; B, calculated[5] (lower limit); C, calculated[5] (upper limit); D, calculated[4]; ●, experiment.[20] This study; symbol, total iodine as I_2/mol dm^{-3}, boric acid/mol dm^{-3}: ○, 4.0×10^{-6}, 1.0×10^{-2}; △, 1.0×10^{-5}, 2.0×10^{-2}; ▽, 1.0×10^{-5}, 1.0×10^{-2}; □, 3.0×10^{-5}, 1.0×10^{-2}; ◇, 6.0×10^{-5}, 1.0×10^{-2}.

$$\log K(T) = 1388/T - 0.2445T + 308.4 \log T - 749.1 \quad \text{(III)}$$

where the units of K and T are mol^2 dm^{-6} and K, respectively.

Values for the rate constant for reaction (2) are summarized in table 2. The effect of this disproportionation was slight in the low-temperature region and the accuracy of the I_2 analysis was 2×10^{-7} mol dm^{-3} in the experiments. Therefore, evaluation could be carried out over a limited temperature range, typically above 80 °C. It has been pointed out that this rate constant depended on such factors as temperature, pH and boric acid concentration.[1,11,13] There are no data using similar temperatures, pH and boric acid concentrations with which the new data here can be directly compared. Toth *et al.*[11] have measured the rate constant in 0.23 mol dm^{-3} boric acid at temperatures from 20 to 150 °C using an indirect method and their data at pH 6 agree with ours (pH = 5.6 [boric acid] = 0.01 mol dm^{-3}) within a factor of 2.

Conclusions

The equilibrium constant for iodine hydrolysis at elevated temperatures was estimated by comparing experimental and simulated results. The following results were obtained.

(1) A computer program was developed by considering 11 normally accepted reactions in I_2/I^- solution, to simulate the I_2 concentration change at high temperatures.

(2) Experiments were performed to investigate the temperature dependence of the extinction coefficient, ε, of I_2 in aqueous solution. The ε value may be expressed by

$$\varepsilon(T) = 1000 - 0.81T$$

where the units of ε and T are dm^3 mol^{-1} cm^{-1} and K, respectively. This enabled I_2 concentration measurements to be made at elevated temperatures by absorption spectroscopy.

(3) The time dependence of the I_2 concentration in dilute solution was measured up to 120 °C from *ca.* 5 min after

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mixing. The results were compared with simulation results and the equilibrium constant K for I_2 hydrolysis was estimated. It was concluded that the K value at temperatures between 25 and 120 °C may be expressed by

$$\log K(T) = 1388/T - 0.2445T + 308.4 \log T - 749.1$$

where the units of K are $\mathrm{mol^2\ dm^{-6}}$.

(4) The rate constant for HOI disproportionation was also evaluated and the results agree with those of Toth *et al.*[11]

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