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THE HYDROLYSIS OF IODINE: EQUILIBRIA AT HIGH TEMPERATURES*

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The hydrolysis (or disproportionation) of molecular iodine to form iodate and iodide ions has been studied by emf measurements over the temperature range, 3.8 to 209.0°C. The interpretation of these results required a knowledge of the formation constant for triiodide ion and the acid dissociation constant of iodic acid, both of which were measured as a function of temperature. The resulting thermodynamic data have been incorporated into a general computer model describing the hydrolysis equilibria of iodine as a function of initial concentration, pH and temperature.

1. INTRODUCTION

The Three Mile Island nuclear accident has focussed renewed attention on the behavior of iodine in aqueous solution. For it was subsequently realized that hydrolysis of iodine in either of its volatile forms, namely molecular iodine I_2 and hypoiodous acid HOI, would substantially reduce the release of ^{131}I to the atmosphere by converting them to the non-volatile ionic forms, iodate (+V) and iodide (-I). Although individual reactions within the matrix of iodine hydrolysis reactions have been extensively studied under ambient conditions, the key disproportionation [equation (3) in the sequence shown below] has been neglected with only one investigation involving two experiments being reported[1]. Turner[2] demonstrated that attempts to estimate the temperature dependence of this reaction based on various thermodynamic assumptions lead to widely differing values for the equilibrium constant at high temperatures (e.g., at 150°C the predicted values differ by 16 orders of magnitude).

Although radiolysis, redox and photochemical processes, as well as interaction with organic radicals, undoubtedly perturb the hydrolysis in a nuclear accident setting, an exact knowledge of the thermodynamic parameters for the principal hydrolysis equilibrium is essential in establishing a model for iodine behavior. Similarly, the kinetics of iodine hydrolysis are important, particularly at low temperatures and low pH values where the rates are slow. Although this aspect will not be addressed here, an experimental program to measure these kinetics has been completed at our laboratory.

In formulating the equilibrium model[3], the following reactions were considered:

$$I_2 + I^- \rightleftarrows I_3^- \quad (1)$$

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

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

$$HOI \rightleftarrows OI^- + H^+ \quad (4)$$

$$HIO_3 \rightleftarrows IO_3^- + H^+ \quad (5)$$

$$H_2OI^+ \rightleftarrows HOI + H^+ \quad (6)$$

$$I_2 + H_2O \rightleftarrows I_2OH^- + H^+ \quad (7)$$

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$$I_2OH^- \rightleftharpoons I_2O^{2-} + H^+ \qquad (8)$$

$$H_2O \rightleftharpoons OH^- + H^+ \qquad (9)$$

$$I_2(\text{vapor}) \rightleftharpoons I_2(\text{aqueous}) \qquad (10)$$

It should be noted that in our initial model[3], which was based solely on the avialable literature data, species such as HIO_3, H_2OI^+ and I_2O^{2-} were found to be insignificant (i.e., <0.01% of the total iodine present) under the conditions pertinent to nuclear accident scenarios, viz. initial iodine and iodide concentrations of 10^{-3} to 10^{-7} gatom/L, pH values from 5 to 10, and temperatures from 25 to 150°C. However, the equilibria pertaining to the species are retained in the model for the sake of completeness. As new experimental results for equations (1), (3) and (5) will be presented in this paper, a brief account of the origin and form of the expressions used to describe the temperature dependence of the remaining equilibrium constants is needed.

The combined data[4-8] for equation (2), spanning a temperature range of 0 to 56°C, were fitted by the equation,

$$\ln K_2 = -1392.9/T - 44.764 + 0.070692T$$

where T represents the temperature in degrees Kelvin and the subscript refers to the reaction to which the equilibrium constant is assigned.

Equation (4) was modeled after the temperature dependence for the acid dissociation of HOBr[9], but adjusted to give the measured value of K_4 for HOI at 25°C.[10] The equilibrium expression for this equation is as follows:

$$\log K_4 = 29688/T + 81.840 \ln T - 0.089649T - 2.0468 \times 10^6/T^2 - 526.75$$

Data are available[8,11] at only two temperatures for equation (6) and hence a linear expression must be used. However, because the charge is the same on both sides of this equation, the heat capacity change should be minimal[12]. This point will be elaborated on in the ensuing discussion.

$$\log K_6 = -2.92/T + 8.27$$

The heats of reaction for equations (7) and (8) are unknown and therefore the equilibrium constants were fixed at their 25°C values, 1.4×10^{-10} and 0.045, respectively.[10]

The dissociation constant for water, K_9, was taken from Marshall and Franck[13], i.e.,

$$\log K_9 = -4.098 - 3245.5/T + 2.2362 \times 10^5/T^2 - 3.984 \times 10^7/T^3 + (13.957 - 1262.3/T + 8.5641 \times 10^5/T^2) \log D_w$$

where D_w represents the density of water and is calculated[14] as follows:

$$D_w = 1.0017 - 2.36582 \times 10^{-5}t - 4.77122 \times 10^{-6}t^2 + 8.27411 \times 10^{-9}t^3$$

where t is the temperature in °C.

The distribution coefficient for iodine between the aqueous and vapor phases has been measured by numerous experimentalists.[7,15] The results of these two studies[15,16] can be best fit by the equations:

$$\log K_{10} = 4220.5/T - 19.991 + 0.02583T \qquad (t < 112°C)$$

$$\log K_{10} = 5615.4/T - 25.1798 + 0.02990T \qquad (t > 112°C)$$

As HOI has not been detected in the vapor phase as yet, only lower limits can be suggested for its distribution coefficient (e.g., 10^4 at 22°C).[16]

2. EXPERIMENTAL

2.1 EMF Measurements

The cell used to determine the equilibrium constant for equation (3) can be represented as follows:

$$Pt|\ I_2(m_L), KI(m_{L1}), HClO_4(m_{L2})\|\ HClO_4(m_{R2}), KIO_3(m_{R1}), I_2(m_R)|\ Pt$$

Details of the equipment and procedure are given elsewhere.[17] Essentially the cell consisted of two concentric compartments, each containing the solutions shown above. Three experiments were carried out with I_2 solutions of simply HI and HIO_3, respectively. The ionic strengths of these solutions, generally <0.1 m, were matched as closely as possible to minimize the liquid junction potential. The actual liquid junction consisted of a porous glass plug. Platinum electrodes completed the circuit with the electrode in the iodate solution being coated with platinum black. The solutions were stirred magnetically throughout the experiment. The cell was initially purged with argon and kept lighttight.

The key to this method was to allow the iodine to distribute between the two solutions via the gas phase. This process, as well as the equilibration of the I_2/IO_3^- couple, required up to five days at 25°C, but was complete within 24 hrs at 200°C. Upon attaining equilibrium, as indicated by a constant potential reading, samples were withdrawn from both solutions: the iodine concentration, m_R, was determined by spectrophotometry using the absorption maximum at 460 nm (ε = 730.9 M^{-1} cm^{-1});[18] the total iodine, m_L, iodate, m_{R1}, and iodide, m_{L1}, concentrations were measured by potentiostatic coulometry; and the proton concentrations, m_{L2} and m_{R2}, were determined by titration with standard NaOH solutions. Twenty-two experiments were carried out over the temperature range 3.8 to 209.0°C.

2.2 Spectrophotometric Measurements

The triiode formation equilibrium, equation (1), was also studied 'in situ' by spectrophotometry over the temperature range 15.3 to 44.7°C.[18] The wavelengths investigated were 370, 350 and 288 nm. The iodine concentration was maintained at 5 × 10^{-5} m, while the iodide concentration was varied from 10^{-3} to 0.02 m, with at least nine measurements within this range at each temperature.

2.3 Solubility

The acid dissociation constant for iodic acid, equation (5), was determined from the difference in solubility of $TlIO_3$ in 0.1 m $NaClO_4$ (10^{-4} m $HClO_4$) and 0.1 m $HClO_4$ over the temperature range 2.2 to 75.0°C. The solutions were analyzed for thallium and iodate by potentiostatic coulometry, the details of which are described elsewhere.[19] Experiments at 100°C indicated that some oxidation of Tl(I) to Tl(III) by iodate had occurred and hence this imposed an upper limit on the temperature range that could be effectively investigated.

3. RESULTS AND DISCUSSION

The operating conditions in the emf experiments imposed a number of constraints on treating the equilibrium data pertaining to equation (3). Firstly, the coexistence of iodine and iodide ions at millimolal levels within the cell resulted in the formation of substantial concentrations of triiode ion. Thus, in order to calculate the molalities of free iodide and iodine, a knowledge of the thermodynamics of I_3^- formation is necessary. This reaction has been well studied in the past,[20] but only over a narrow temperature range such that the large uncertainty in the ΔC_p (reported values vary from -263 to +97 J K^{-1} mol^{-1} at 25°C) makes reliable extrapolation to higher temperatures impossible. Fortunately, this information is provided directly from the analyses of the solutions in the cell.

At equilibrium, the free iodine molality in the iodide solution is to m_R, the iodine molality in the iodate soluiton, due to the partitioning of iodine between the two solutions which are at the same temperature and ionic strength. Hence, the molality of I_3^- = $m_L - m_R$ and the molality of free I^- = $m_{L1} - m_{I_3^-}$. Independent determinations of K_1 were obtained from 'in situ' spectrophotometric observations of the absorption due to I_2, I_3^- and I^-. The complete data set, encompassing 21 experiments over the temperature range 3.8 to 209.0°C,[18] can best be described by the equation:

$$\log K_1 = 555.0/T + 7.355 - 2.575 \log T$$

which is the form used to describe the temperature dependence of K_1 in the new model. The molal thermodynamic quantities at 25°C associated with these parameters are $K_1 = 690 \pm 10$, $\Delta H_1° = -17.0 \pm 0.6$ kJ mol^{-1}, $\Delta S_1° = -0.6 \pm 0.3$ J K^{-1} mol^{-1}, and $\Delta C_{p,1}° = -21 \pm 8$ J K^{-1} mol^{-1}.[18]

The second constraint arose from the need to correct for the degree of association of iodic acid at the relatively high acidity of the solutions in the emf experiments, viz. generally 0.01 to 0.10 m. Although previous calorimetric measurements at 25°C[21] and solubility measurements of $AgIO_3$ from 25 to 35°C,[22] provided the necessary thermodynamic quantities for the association of HIO_3, a new study was undertaken based on the solubility of $TlIO_3$ at temperatures from 2.2 to 75.0°C.[19] The wider temperature range, the precision of potentiostatic coulometry, and the ability to analyze accurately for both Tl^+ and IO_3^- should give this work inherent advantages over the previous solubility studies. Accuracy in estimating K_5 at high temperatures is particularly important because iodic acid becomes weaker with increasing temperature and hence the correction of the observed total iodate and hydrogen ion molalities becomes more significant. Using the reported value for K_5 at 25°C,[23] mean ionic activity coefficients for $TlIO_3$ and HIO_3 were calculated in both the acidic and neutral media. The results of the nine experiments performed over the 73°C temperature range can be represented by the equation:

$$\log K_5 = -657.45/T + 21.589 - 8.158 \log T$$

At 25°C, the molal thermodynamic parameters are, $K_5 = 0.157$, $\Delta H_5° = -7.7 \pm 0.3$ kJ mol^{-1}, $\Delta S_5° = -41.0 \pm 1.3$ J K^{-1} mol^{-1}, and $\Delta C_{p,5}° = -68 \pm 22$ J K^{-1} mol^{-1} [19] (c.f. $\Delta H_5° = 02.8 \pm 0.5$ kJ mol^{-1}, $\Delta S_5° = 24.7$ J K^{-1} mol^{-1}, and $\Delta C_{p,5}° = -34 \pm 8$ J K^{-1} mol^{-1})[21]. However, in the model equation (5) was written in its basic form,

$$\log K_5 = 3263.8/T + 2.2633 + \log K_9$$

which is equivalent to assuming that $\Delta C_p°$ is zero for this reaction and that $\Delta C_{p,5}° = \Delta C_{p,9}°$. This is in keeping with all the previous results obtained for other acids.

The third constraint deals with estimating the liquid junction potential in the cell. This was approximately by the Henderson equation.[23,24] The maximum correction invoked by this treatment was 3.8 mV, with the average being less than 1 mV.

The final constraint is limited by the ability to predict the activity coefficients of the species involved in the equilibrium expression for K_3. In the absence of relevant experimental values, and based on the temperature dependence of a wide variety of ions, the individual ionic activity coefficients can best be estimated from the revised Davies equation.[25] Based on iodine solubility measurements in $NaClO_4$ media at 25°C, the activity coefficient of aqueous iodine was set at unity.

The final calculated values of log K_3 vs. 1/T are shown in Figure 1. The smooth line is the result of a least-squares fit of the data according to the equation,

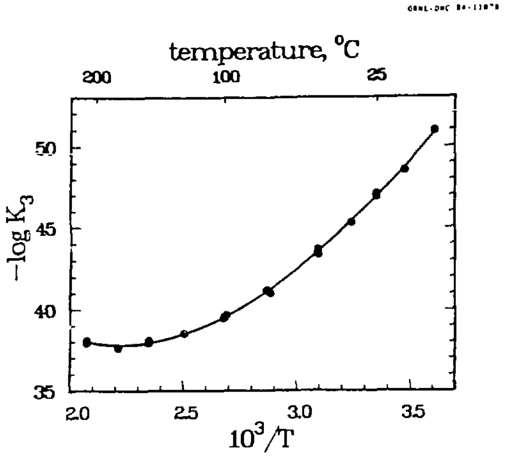

FIGURE 1

Plot of the logarithm of the molal equilibrium constant, K_3 vs. 1/T.

$$\log K_3 = -42304/T + 631.24 - 216.73 \log T$$

from which the following molal thermodynamic quantities at 25°C were derived,[17] $\log K_3 = -46.93 \pm 0.22$, $\Delta H_3° = 272.6 \pm 2.8$ kJ mol^{-1}, $\Delta S_3° = 16 \pm 9$ J K^{-1} mol^{-1}, and $\Delta C_{p,3}° = -1802 \pm 41$ J K^{-1} mol^{-1}. The value of log K_3 at 25°C is in approximate agreement with the interpolated value obtained by Lundberg et al.[1] of -45.01.

Again, this reaction can be formulated in terms of anion (i.e. in its basic form) as follows,

$$3I_2 + 6OH^- \rightleftharpoons IO_3^- + 5I^- + 3H_2O \qquad (11)$$

to reduce the heat capacity term by balancing the charges on both sides of the equation. Note that the reaction in this form should also be far less influenced by changes in the ionic strength. The data expressed in this form are shown in Figure 2 where the smooth curve can be represented by the equation:

$$\log K_{11} = -6578.8/T + 248.25 - 76.431 \log T$$

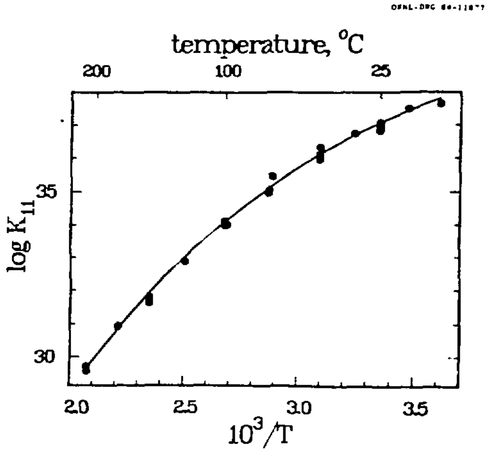

FIGURE 2

Plot of the logarithm of the molal equilibrium constant, K_{11}, vs. 1/T.

The later equation is the one used in the speciation model.

The results of combining these new equations into the previous computer model[3] are illustrated in Figures 3 and 4. The concentrations of 10^{-4} to 10^{-6} were chosen to represent the upper and expected concentrations, respectively, in many nuclear accident scenarios. The speciation was calculated in each case assuming that these concentrations of molecualr iodine were introduced at the appropriate temperature at any pH between 0 and 11 and allowed to hydrolyze to its final equilibrium value. The main features of diagrams is that increasing temperature destabilizes I_2 with respect to IO_3^- and I^- at a given pH as dictated by equation (3). Secondly, decreasing the initial iodine concentration has the same effect. Thirdly, increasing temperature and decreasing concentration both tend to stabilize HOI to substantial levels at lower pH. It must be rememebered tha the HOI equilibria were only measured at lower temperatures and hence these results above 60°C are based on extrapolation.

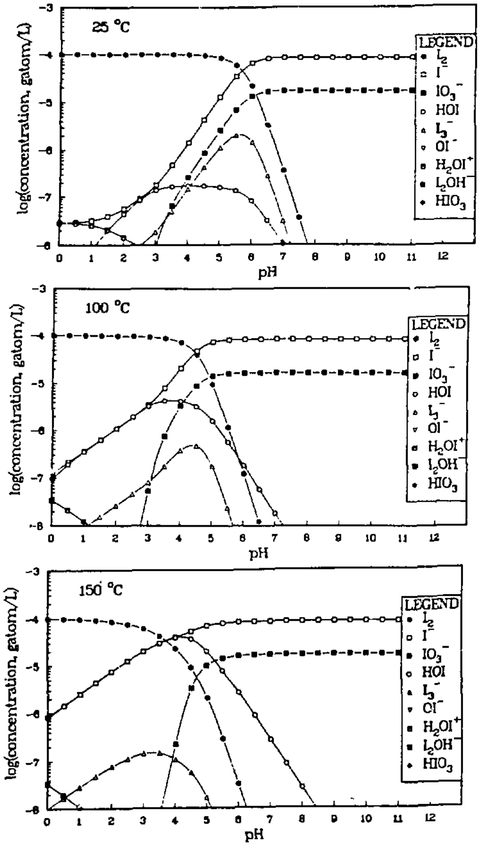

FIGURE 3

Speciation diagrams at initial iodine concentrations of 10^{-4} gatom/L as a function of temperature and pH.

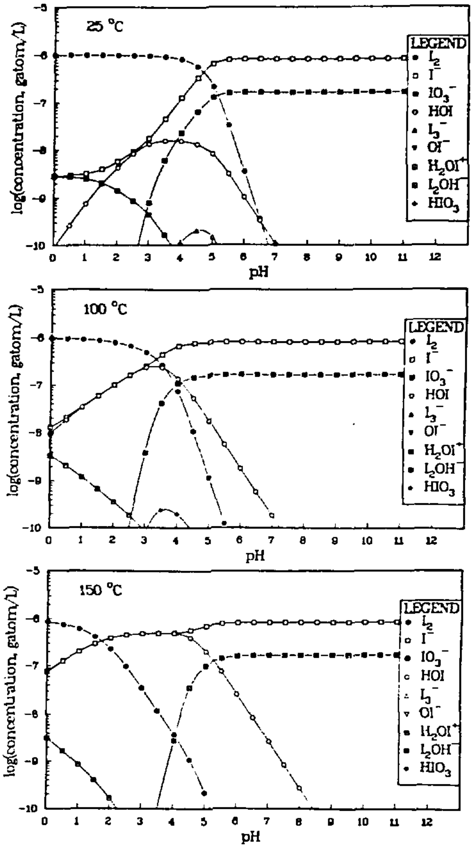

FIGURE 4

Speciation diagrams at initial iodine concentrations of 10^{-6} gatom/L as a function of temperature and pH.

4. CONCLUSIONS

The principal equilibrium involving aqueous iodine has been established quantitatively as a function of temperature for the first time. A computer model for the aqueous chemistry of iodine at equilibrium in the absence of added redox partners has been adapted to include these new data. The concentration levels of ten aqueous iodine species, as well as vapor phase iodine, can be estimated as a function of initial iodine, iodide and iodate concentrations, temperature and pH. These conditions encompass those anticipated in nuclear accident scenarios.

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