The solvent deuterium isotope effect on the dissociation constant of iodic acid*

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Dedicated to Professor Rudolf Signer

Summary

The solubilities of hydrated and deuterated copper (II) iodate in $HClO_4$–H_2O and $DClO_4$–D_2O solutions respectively, were measured at 1, 15, 25 and 35 °C, the perchloric acid concentrations ranging from 0 to 1.0 m. These experimental results were used to calculate the solvent deuterium isotope effect, ΔpK, on the dissociation constants of HIO_3 and DIO_3. At ionic strength $I = 1.0$ m (Li) ClO_4 the following values were obtained, $\Delta pK = pK\ (D_2O) - pK\ (H_2O)$: 0.359 ± 0.027 (1°), 0.323 ± 0.015 (15°), 0.323 ± 0.047 (25°), 0.380 ± 0.025 (35°).

Introduction

The equilibrium isotope effect on acid constants, resulting from a replacement of H_2O by D_2O as a solvent, is usually defined as follows:

$$\Delta pK = pK\ (D_2O) - pK\ (H_2O). \qquad (1)$$

The values observed experimentally for acids weaker than the hydrated proton are always positive and cover a range[1] of $0.2 < \Delta pK < 0.9$. This well-known fact, which is at least qualitatively predicted by statistical mechanics[2],

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has an important application to the study of reaction mechanisms. It can be shown that inverse solvent isotope effects on reaction rates, $k(D_2O)/k(H_2O) > 1$, are generally indicative of acid-base equilibria prior to the rate determining step[2]. A remarkably high value of $k(D_2O)/k(H_2O) = 9.8$ has been reported[3] for reaction (A) between iodate and iodide

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

which proceeds according to the rate law (2)[4]

$$v = k[H^+]^2\,[IO_3^-]\,[I^-]^2. \qquad (2)$$

The fraction of the overall kinetic isotope effect originating in ΔpK of iodic acid can be estimated only if the relevant K values are known for the same conditions as for the kinetic investigation.

The protolysis of HIO_3 has been investigated very carefully[5]; however, no accurate method has been developed so far for extrapolation from the "thermodynamic" pK to pK values valid at the high ionic strengths usually employed in kinetic work. The dissociation constant of DIO_3 has been determined by conductimetric measurements. The actual reliability of the value reported is hard to estimate, however, since it can not be recalculated from the information given[1].

In the present work an attempt was made to determine the acid constants of HIO_3 and DIO_3 at high ionic strengths in H_2O and D_2O respectively, using the attractively simple copper iodate solubility method described by Ramette[6].

Experimental

Materials

Copper iodate hydrate and deuterate were prepared according to the procedure described by Ramette and Broman[7]. The X-ray powder diffraction pattern of the hydrate form was found to be identical with bellingerite, $Cu_3(IO_3)_6 \cdot 2\,H_2O$[8]. The X-ray powder diffraction pattern of the deuterate form is quite similar, so we concluded that it is $Cu_3(IO_3)_6 \cdot 2\,D_2O$. $DClO_4$ standard solution (approx. 1 m $DClO_4$) was prepared by an ion exchange method. An exchange resin (Dowex 50 W × 8, 20/50 mesh) was deuterated by upflow passage of D_2O through the column containing the resin in the H^+-form. The progress of deuteration was followed by measuring the density of the effluent. Then, $NaClO_4$, dried at 180°, was dissolved in D_2O and passed down through the D^+-form of the resin. The breakthrough of Na^+ ion was monitored by flame photometry. The resulting $DClO_4$ solution contained less than 0.01% Na and less than 0.2% H.

Lithium perchlorate was prepared from lithium carbonate and perchloric acid and purified by several recrystallizations. Deuterium oxide (> 99.8% D) was obtained from the E.I.R. Würenlingen. All chemicals used were reagent grade. Light water for solution preparation was double-distilled using an all quartz apparatus.

Procedures

Stock solutions of 1.0 m $LiClO_4$ and 1.0 m $HClO_4$ in H_2O and 1.0 m $DClO_4$ in D_2O were prepared. Mixtures of these solutions with varying H^+ and D^+ concentrations were made on a weight basis so as to maintain the molal ionic strength constant ($I = 1.0$ m).

An excess of solid copper iodate in the hydrated or deuterated form respectively, was placed in glass ampoules and the appropriate solutions were added. The ampoules were sealed off and shaken in a water-thermostat kept at 1, 15, 25 or 35° within ± 0.1°. After equilibration the saturated solutions were separated from the solid phase by millipore filtration. The time interval required for equilibration was estimated from preliminary experiments. The amount of copper iodate dissolved was determined iodometrically. X-ray powder diffraction patterns obtained from the solid phase before and after the equilibration process showed no significant differences. Random samples of the heavy water experiments were taken to check the dilution with ordinary water during the course of manipulations. The D_2O content determined photometrically[9] was always larger than 98%.

Calculation of results

Assuming constant activity coefficients and negligible $CuIO_3^+$ formation the calculations of the iodic acid constants were based on the equations

$$[H^+]\ [IO_3^-] = [HIO_3] \cdot Ka. \qquad (3)$$

$$[Cu^{2+}]\ [IO_3^-]^2 = Kso. \qquad (4)$$

$$[IO_3^-] + [HIO_3] = 2\,[Cu^{2+}]. \qquad (5)$$

$$[H^+] + [HIO_3] = [H^+]_i. \qquad (6)$$

$[H^+]_i$ indicates the initial H^+ (D^+)-concentration, whereas the other bracketed terms refer to equilibrium concentrations. Combining equations (3), (4) and (5) leads to

$$2\,[Cu^{2+}]^{3/2} = Kso^{1/2} + Kso^{1/2}\,Ka^{-1}[H^+]. \qquad (7)$$

The actual H^+-concentration, $[H^+]$, was not directly available from the experiments, but was determined by a series of successive approximations. A preliminary value of Ka was obtained by neglecting $[HIO_3]$ in eq. (6). This Ka value was used to calculate an improved H^+-concentration with the aid of eq. (8).

$$[H^+] = ([H^+]_i - Ka)/2 - [Cu^{2+}] + \sqrt{Ka\,[H^+]_i + \{([H^+]_i - Ka)/ - 2\,[Cu^{2+}]\}^2}. \qquad (8)$$

Now, Ka was recalculated and so on, until after 3 to 5 cycles the results converged.

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Table 1. Solubility product of copper iodate and dissociation constant of iodic acid in D_2O and H_2O respectively

The values were calculated on the basis of molal concentrations. Errors given for pK values are 2σ, for ΔH and ΔS are σ (σ is the standard deviation)

Temperature (°C)	$pKso\,(D_2O)$	$pKso\,(H_2O)$	$\Delta pKso$	$pKa\,(D_2O)$	$pKa\,(H_2O)$	ΔpKa
1	6.821 ± 0.036	6.366 ± 0.025	0.455 ± 0.044	0.574 ± 0.020	0.215 ± 0.018	0.359 ± 0.027
15	6.588 ± 0.019	6.207 ± 0.015	0.381 ± 0.024	0.602 ± 0.011	0.297 ± 0.010	0.323 ± 0.015
25	6.411 ± 0.080	6.083 ± 0.030	0.328 ± 0.085	0.629 ± 0.043	0.306 ± 0.020	0.323 ± 0.047
35	6.293 ± 0.021	5.978 ± 0.035	0.315 ± 0.041	0.731 ± 0.011	0.351 ± 0.023	0.380 ± 0.025

Reaction	copper iodate (H_2O) dissolution (B 1)	copper iodate (D_2O) dissolution (B 2)	iodic acid (H_2O) dissociation (C 1)	iodic acid (D_2O) dissociation (C 2)
ΔH_{298} (kcal)	13.3 ± 0.3	18.2 ± 0.7	− 1.50 ± 0.09	− 1.64 ± 0.55
ΔS_{298} (e.u.)	− 38.7 ± 1.1	− 26.7 ± 2.3	− 6.5 ± 0.3	− 8.5 ± 1.9

Once *Kso* and *Ka* are known for different temperatures *ΔH and ΔS* for reactions (B1), (B2), (C1) and (C2) can be evaluated by standard procedures

$$Cu_3(IO_3)_6 \cdot 2\,H_2O_{(s)} \rightleftarrows 3\,Cu^{2+}_{(H_2O,\,I=1)} + 6\,IO^-_{3\,(H_2O,\,I=1)} + 2\,H_2O_{(I=1)}, \quad (B1)$$

$$Cu_3(IO_3)_6 \cdot 2\,D_2O_{(s)} \rightleftarrows 3\,Cu^{2+}_{(D_2O,\,I=1)} + 6\,IO^-_{3\,(D_2O,\,I=1)} + 2\,D_2O_{(I=1)}, \quad (B2)$$

$$HIO_{3\,(H_2O,\,I=1)} \rightleftarrows H^+_{(H_2O,\,I=1)} + IO^-_{3\,(H_2O,\,I=1)}, \quad (C1)$$

$$DIO_{3\,(D_2O,\,I=1)} \rightleftarrows D^+_{(D_2O,\,I=1)} + IO^-_{3\,(D_2O,\,I=1)}. \quad (C2)$$

An HP 2114 B computer was used for the data processing.

Results and discussion

According to eq. (7) $2\,[Cu^{2+}]^{3/2}$ was plotted against $[H^+]$ and $[D^+]$ respectively (see Fig. 1 and 2). Each data pair is the average of 3 to 9 independent determinations[10, 11]. As shown in Fig. 1 and 2, the experimental data fell on straight lines, thus the assumption of constant activity coefficients is valid in the whole range of solvent compositions. This effect is due to the similarity of lithium and hydrogen ions[6, 12].

The thermodynamic data computed from the slopes and intercepts of the straight lines are summarized in the Table 1. Since the measurements were made in a limited temperature range, $\delta \ln K/\delta(1/T)$ was taken to be constant.

The *ΔpK* value of iodic acid obtained at 25° (see Table) agrees reasonably well with the value given by McDougall and F. A. Long[1]. It can be concluded that apart from the protolysis of iodic acid, other acid base equilibria are contributing to the extremely high kinetic solvent isotope effect of reaction (A). Even a rate law with a third order dependence on hydrogen ion concen-

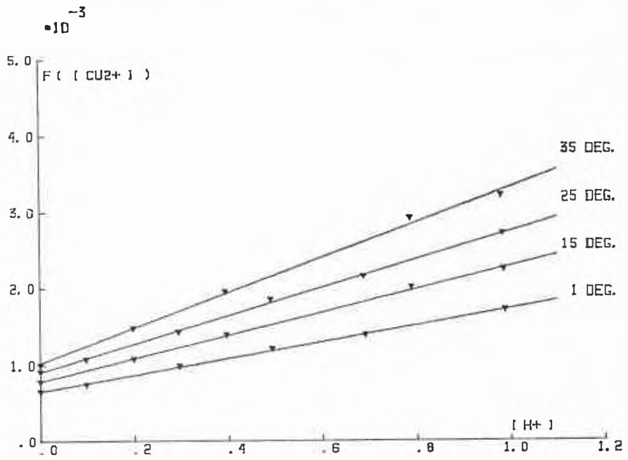

Fig. 1. Solubility of $Cu_3(IO_3)_6 \cdot 2\,H_2O$ in $HClO_4$—H_2O ($I = 1.0$ m [Li] ClO_4). On the ordinate $F([Cu^{2+}]) = 2\,[Cu^{2+}]^{3/2}$ was plotted according to eq. (7). On the abscissa the actual hydrogen ion concentration. $[H^+]$, was plotted

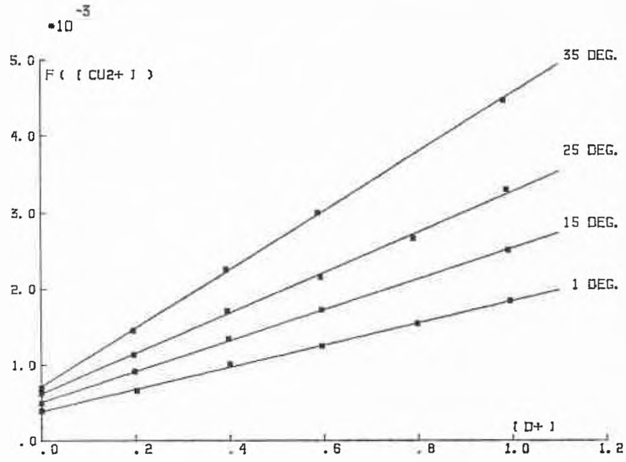

Fig. 2. Solubility of $Cu_3(IO_3)_6 \cdot 2\,D_2O$ in $DClO_4$—D_2O ($I = 1.0$ m [Li] ClO_4). On the ordinate $F([Cu^{2+}]) = 2\,[Cu^{2+}]^{3/2}$ was plotted according to eq. (7). On the abscissa the actual deuterium ion concentration, $[D^+]$, was plotted

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tration would be consistent with $k(D_2O)/k(H_2O) = 9.8$, however, none of the rate laws containing $[H^+]^3$ have been firmly established so far[4].

Similar to previous results[7], the solubility of copper iodate has been found to be lower in D_2O than in H_2O. This can be attributed to an unfavorable enthalpy effect of reaction (B2) as compared to reaction (B1).

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