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# The Solubility Product of Cesium Metaperiodate and a Nuclear Magnetic Resonance Study of the Orthoperiodate–Metaperiodate Dehydration Equilibrium

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The solubilities of cesium metaperiodate in aqueous solutions of pH 1.3–5.8 have been measured at 5.0, 25.0, and 40.0°. The values calculated for $K_{sp}^0$ at these temperatures were $(3.96 \pm 0.17) \times 10^{-4}$, $(2.24 \pm 0.07) \times 10^{-3}$, and $(6.53 \pm 0.04) \times 10^{-3}$. At 25°, $\Delta G_{soln}^\circ = 1.91 \pm 0.05$ kcal/mole, $\Delta H_{soln}^\circ = 13.1$ kcal/mole, and $\Delta S_{soln}^\circ = 37.6$ eu. Evidence was found for a new periodate phase in the system $H_2O$–$CsIO_4$–$CsOH$, and two previously unreported cesium periodate salts were prepared. The equilibrium constant $K_d^0$ and thermodynamic quantities for the reaction $H_4IO_6^-(aq) \rightleftharpoons IO_4^-(aq) + 2H_2O(l)$ have been determined in the temperature range 2–18° by means of a nuclear magnetic resonance technique. The extrapolated value of $K_d^0$ at 25° was found to be 29. The corresponding value of $\Delta G_d^\circ$ was $-2.0 \pm 0.1$ kcal/mole, of $\Delta H_d^\circ$ was $14.8 \pm 1.1$ kcal/mole, and of $\Delta S_d^\circ$ was $56 \pm 4$ eu.

## Introduction

As part of our continuing investigation of the chemistry of periodates, we have studied the preparation and some properties of cesium metaperiodate, which has until now received surprisingly little attention. Wells[1] has reported a method of preparation of $CsIO_4$ and stated that no other periodates were detected in his studies of the $H_2O$–$CsIO_4$–$CsOH$ system. This comment seems to have discouraged further investigation, despite the subsequent isolation of salts in the very similar $KIO_4$–$KOH$–$H_2O$ system having other ratios of iodine to alkali metal ion.[2] Only a single value for the solubility of $CsIO_4$ in water has been reported previously.[3] The authors therefore undertook a study of the solubility of $CsIO_4$ in the pH range 1–6 in order to establish its solubility product constant and also undertook the extension of Wells' preparative studies to more basic solutions.

An explanation of the solubility of a metaperiodate salt, *e.g.*, $CsIO_4$, can never be made solely in terms of cation and metaperiodate anion equilibrium with the solid because metaperiodate ions ($IO_4^-$) undergo changes in hydration and solvolysis upon their solution in water. The equilibria, shown with their equilibrium constants, must be taken into account

$$H_4IO_6^-(aq) \rightleftharpoons IO_4^-(aq) + 2H_2O(l);\ K_d^0 = \frac{(IO_4^-)}{(H_4IO_6^-)}a_{H_2O}^2 \tag{1}$$

$$H_5IO_6(aq) \rightleftharpoons H_4IO_6^-(aq) + H^+(aq);\quad K_1^0 = \frac{(H_4IO_6^-)(H^+)f_1^2}{(H_5IO_6)} \tag{2}$$

$$H_4IO_6^-(aq) \rightleftharpoons H_3IO_6^{2-}(aq) + H^+(aq);\ K_2^0 = \frac{(H_3IO_6^{2-})(H^+)f_2}{(H_4IO_6^-)} \tag{3}$$

$$CsIO_4(s) \rightleftharpoons Cs^+(aq) + IO_4^-(aq);\ K_{sp}^0 = (Cs^+)(IO_4^-)f_1^2 \tag{4}$$

In the above equilibrium constant expressions, the parentheses indicate molar concentration, and $f_i$ is the molar activity coefficient of an ion of charge $\pm i$. The activity coefficients of species of the same charge, positive or negative, are assumed equal. The activity coefficients of neutral species are assumed to be unity.

If $I_t$ is allowed to denote the molar solubility of $CsIO_4$, then on the basis of conservation of matter we may write that

$$I_t = (Cs^+) = (IO_4^-) + (H_4IO_6^-) + (H_5IO_6) + (H_3IO_6^{2-}) \tag{5}$$

Equations 1, 2, 3, and 5 may be combined with eq 4 to obtain

$$K_{sp}^0 = I_t^2 f_1^2 K_d^0 \left[\frac{1}{K_d^0 + 1 + \frac{f_1 a_{H^+}}{K_1^0} + \frac{K_2^0 f_1}{f_2 a_{H^+}}}\right] \tag{6}$$

To calculate a meaningful value of $K_{sp}^0$ from the solubilities of $CsIO_4$ at various pH values, it is apparent that $K_d^0$, $K_1^0$, and $K_2^0$ must be known for the particular temperature. Such values have been previously determined spectrophotometrically[4] and indicated that in the equilibrium shown by eq 1, the metaperiodate species predominated over orthoperiodate. A similar set of constants was used successfully to account for the variations in the solubility of tetraphenylarsonium metaperiodate as a function of pH and temperature.[5] The dominance of $IO_4^-(aq)$ over $H_4IO_6^-(aq)$ has also been claimed as a result of a study of the Raman spectrum of an aqueous solution of $NaIO_4$,[6] which shows three lines assigned to a tetrahedral species and one line assigned to un-ionized $H_5IO_6(aq)$. However, from a study of the infrared spectrum of the solid salt $NaIO_4 \cdot 3H_2O$ and the infrared spectrum of aqueous $NaIO_4$, the conclusion has been drawn[7] that $IO_4^-(aq)$ plays but a minor role in aqueous periodate chemistry and that $H_4IO_6^-(aq)$ and $H_2IO_5^-(aq)$ are in greatest abundance. To gain additional information, we have studied the dehydration equilibrium shown by eq 1 using a nuclear magnetic resonance (nmr) technique. This allows a direct measurement of the concentration

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[1] H. L. Wells, *Am. Chem. J.*, **50**, 278 (1901).

[2] A. E. Hill, *J. Am. Chem. Soc.*, **50**, 2678 (1928).

[3] T. V. Barker, *Trans. Chem. Soc.*, **93**, 15 (1908).

[4] C. E. Crouthamel, A. M. Hayes, and D. S. Martin, *J. Am. Chem. Soc.*, **73**, 82 (1951).

[5] S. H. Laurie, J. M. Williams, and C. J. Nyman, *J. Phys. Chem.*, **68**, 1311 (1964).

[6] H. Siebert, *Z. Anorg. Allgem. Chem.*, **273**, 21 (1953).

[7] N. Keen and M. C. R. Symons, *Proc. Chem. Soc.*, 383 (1960).

of metaperiodate ion which in turn allows calculation of a value of $K_d^0$.

In this paper are reported the solubility product constants for $CsIO_4$ at various temperatures and the thermodynamic quantities calculated therefrom. Also included are the equilibrium constants for the orthoperiodate–metaperiodate ion equilibrium in the temperature range 2–18° and the corresponding thermodynamic quantities.

## Experimental Section

**Cesium Metaperiodate, $CsIO_4$.**—A variation of Wells' method[1] was used. A concentrated solution of 72 g of CsOH (Penn Rare Metals, 99.9%) in 100 ml of double-distilled water was allowed to react with a solution of 108 g of $H_5IO_6$ (Matheson Coleman and Bell, minimum assay as $H_5IO_6$, 99.5%) in 100 ml of double-distilled water. The resulting solution was acid to litmus. The $CsIO_4$ product formed immediately as a fine white powder, which was recrystallized three times from 100 ml of double-distilled water and dried to constant weight at 60°. No oxidation of $H_2O$ by periodate was noted during preparation; starch–iodide paper was used for this test. *Anal.* Calcd for $CsIO_4$: I, 39.19. Found: I, 39.21.

**Tetracesium Dihydrogen Decaoxodiiodate(VII) Octahydrate, $Cs_4H_2I_2O_{10}\cdot 8H_2O$.**—The preparation of $K_4I_2O_9\cdot 9H_2O$,[2] recently shown to be $K_4H_2I_2O_{10}\cdot 8H_2O$,[8] led to the attempt to make the analogous cesium salt. To a solution of 1.06 g of CsOH in 10 ml of water, solid $CsIO_4$ was added such that the final mole ratio of $CsIO_4$ to CsOH was 1.5. The solution was stirred for 4 hr and then filtered free of unreacted $CsIO_4$. Solvent water was removed by heating at 50° until fine crystals were noticed to form in the reaction vessel. The solution was then cooled in an ice bath and the resulting crystals were collected on a sintered-glass crucible and dried by drawing air through the crucible. *Anal.* Calcd for $Cs_4H_2I_2O_{10}\cdot 8H_2O$: I, 23.25. Found: I, 23.3.

**Cesium Enneaoxodiiodate(VII), $Cs_4I_2O_9$.**—Solid $Cs_4H_2I_2O_{10}\cdot 8H_2O$ was heated at 60° to constant weight and the 14.77% weight loss was found to correspond to the loss of 9 moles of $H_2O$ per mole of $Cs_4H_2I_2O_{10}\cdot 8H_2O$. The resulting solid analyzed as $Cs_4I_2O_9$. *Anal.* Calcd for $Cs_4I_2O_9$: I, 27.30. Found: I, 27.2.

**Analysis of Materials.**—The absence of foreign metal ions, notably $K^+$ and $Rb^+$, in the $CsIO_4$ prepared for use in the present investigation was established by flame photometric methods. No emission above background was observed at 767 and 780 mμ, and therefore neither of these elements was present in appreciable quantities.[9] Iodine was determined by dissolving weighed samples of salt in water, adding $H_2SO_4$ and NaI, and then titrating the liberated iodine with standard thiosulfate using starch as an indicator. Iodine was also determined by reducing periodate solution with $SO_2$, boiling to remove excess $SO_2$, and then adding $AgNO_3$ to precipitate AgI. The solid AgI was collected in a porcelain filtering crucible, dried, and weighed. Results from both methods were in good agreement.

**Solubility Measurements.**—Samples of solid $CsIO_4$ were placed in glass-stoppered Pyrex equilibration tubes of 50-ml capacity, and appropriate amounts of solutions of 0.1000 $M$ $HNO_3$ and 0.1000 $M$ $NaNO_3$ were added to fill the tube and give the desired pH. The samples were then stoppered, sealed with Parafilm, and mounted on a frame rotating about a horizontal axis. The entire rotor was enclosed in an insulated thermostated water bath. After equilibration for periods in excess of 72 hr (24 hr was sufficient to ensure attainment of equilibrium), aliquot portions of the samples were withdrawn from the equilibration tubes into pipets adjusted to the same temperature. The pipets were fitted with a very small cut off sintered-glass filtering crucible to prevent uptake of crystals. Thirty milliliters of a 6 $N$ $H_2SO_4$ solution was added to the aliquot portions of the sample, and the resulting solutions were placed in an ice bath for 0.5 hr. Solid NaI was added, and the resulting $I_2$ solutions, still at ice-bath temperature, were titrated with standard $Na_2S_2O_3$ solution using a starch solution as indicator. It was found during the actual determinations, in concurrence with preliminary experiments performed in this laboratory, that $NO_3^-(aq)$ does not oxidize $I^-(aq)$ at ice-bath temperatures during the time interval employed for titrations. The NaI was brought into contact with the periodate solutions for only 10–30 sec prior to titration in order to minimize losses due to volatilization of $I_2$. The precision obtained in all titrations indicated that the long equilibration between iodide and periodate suggested in the literature[10,11] is not necessary. A series of confirmatory experiments was performed to show that the reaction of periodate with iodide ion is complete under the conditions described. It was found that the titrated samples gave evidence of oxidation of excess iodide by nitrate ion or atmospheric oxygen only when allowed to stand for several days at room temperature.

All pH values were determined with a Beckman Model G pH meter, using standard buffer solutions (pHydrion) to calibrate the instrument. To avoid precipitation of $KIO_4$ in the capillary of the saturated calomel electrode of the pH meter, the KCl solution was replaced with a 4.16 $M$ NaCl solution.

**Nuclear Magnetic Resonance Study.**—The magnet used was obtained from Alpha Scientific and was employed with an Alpha Scientific AL150-30A magnet power supply having a stated regulation of 1 part in $10^5$. The magnet was operated at 8.5 kG, at which setting $^{127}I$ has a resonance frequency of 6.9 MHz. A Varian V4230 4–8-MHz probe was employed and was connected to a Varian V4210A variable-radiofrequency unit. The latter was operated at power levels sufficiently low to avoid saturation of the $^{127}I$ signals. The power supply for the radiofrequency unit was a Varian 4260B power supply. An Eico HF-89 power amplifier provided the modulation current for the probe; the modulation field amplitude was adjusted by means of a series of calibrations so that true derivative curves were obtained. The output of the Varian radiofrequency unit was also fed into a Princeton Applied Research Lock-in Amplifier, Model JB-5, operating at 400 Hz. The signal was displayed on a strip recorder as the derivative of the absorption curve. Cooling of the samples was achieved by passing dry, cool air through the probe and allowing it to circulate around the sample. Periodate samples in nmr sample tubes were precooled in an ice bath and then placed in the probe and allowed to warm slowly in the cold air flow. It was found by inspection of spectra from standard iodide solutions that the quality factor of the coil of the probe was unchanged by passing cold air through the probe under the experimental conditions employed by us. Temperatures were determined between each spectrum by means of a thermocouple placed in a well inside the sample tube. The temperatures recorded for the runs were believed accurate to ±0.3°

In preparation of the samples studied, reagent grade sodium periodate (Matheson Coleman Bell) and sodium iodide (Baker Analyzed) were used without further purification. All samples, standard iodide as well as periodate, were pipetted as aliquot portions into the Pyrex test tubes which served as sample tubes. Standard iodide solutions were made by weighing solid sodium iodide into volumetric flasks and then adding sufficient water to dissolve the salt and to dilute to volume. Periodate solutions were standardized by pipetting aliquot portions into acidified iodide solutions and then titrating the liberated iodine with standard thiosulfate solution. The pH values of the periodate solutions were determined as above. The nmr spectra were measured with a draftsman's ruler to ±0.02 cm, which is ±5% of the interval measured.

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(8) A. Ferrari, A. Braibanti, and A. Tiripicchio, *Acta Cryst.*, **19**, 629 (1965).

(9) J. A. Dean, "Flame Photometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p 163 ff.

(10) J. R. Partington and R. K. Bahl, *J. Chem. Soc.*, 1086 (1934).

(11) E. Kimmins, *ibid.*, 356 (1887).

## The Nmr Study of the $H_4IO_6^-(aq)$–$IO_4^-(aq)$ Equilibrium

**Broadening of Nmr Signals.**—The expression for the broadening of nmr spectral lines of nuclei with quadrupole moments has been given elsewhere[12] and is of the form

$$\Delta\omega = \left(\frac{2\pi^3\eta a^3}{5kT}\right)\left(\frac{2I+3}{I^2(2I-1)}\right)\left(1+\frac{\epsilon^2}{3}\right)(e^2qQ)^2 \qquad (7)$$

wherein $\Delta\omega$ is the signal broadening in radians per second, $eQ$ is defined as the electric quadrupole moment of the nucleus, $q$ is the electric field gradient at the nucleus, $a$ is the radius of the sphere which the molecule (ion) is assumed to be, $\eta$ is the bulk viscosity of the solvent, $I$ is the nuclear spin, $k$ is the Boltzmann constant, $T$ is the absolute temperature, and $\epsilon$ is the asymmetry parameter defined as

$$\epsilon = \frac{q_{xx} - q_{yy}}{q_{zz}} \qquad (8)$$

It may be seen from eq 7 and 8 that the breadth of an nmr spectral line is strongly dependent upon the symmetry of the molecule of which the nucleus is part through the magnitudes of $q$ and $\epsilon$. For a tetrahedral molecule, $q$ may be shown to be zero at the central atom. For molecules with a twofold or higher axis collinear with the $z$ axis, $\epsilon$ will be zero at an atom on the axis.[13]

To measure the equilibrium constant between $H_4IO_6^-(aq)$ and $IO_4^-(aq)$, the concentrations of the two species must be known in the same solution. The nmr signal from tetrahedral $IO_4^-(aq)$ will be unbroadened by the quadrupole relaxation term shown in eq 7, whereas the signal from $H_4IO_6^-(aq)$ should be considerably broadened. This broadening, with its concomitant lessening of the $H_4IO_6^-(aq)$ signal amplitude, should render the nmr spectrum of $H_4IO_6^-(aq)$ unobservable.

**Quantitative Analysis by Nmr Techniques.**—For an aqueous sodium iodide solution, we find that the integrated intensity of the derivative of the absorption mode signal may be related to the iodide concentration through the equation[14,15]

$$(I^-) = TK(\Delta\omega_{max})^2D_{max} \qquad (9)$$

The quantities $D_{max}$ and $\Delta\omega_{max}$ are shown graphically in Figure 1 and $K$ is a constant containing terms related to the iodine nucleus in any environment and terms related to the experimental conditions. If these experimental conditions (resonance frequency, sample volume, radiofrequency field, and magnetic field strength) are held constant while the spectra of both a standard iodide solution and a periodate solution are taken, then the concentration of species (denoted "P") showing an observable resonance in the periodate solution, *e.g.*, $IO_4^-(aq)$, may be calculated by the expression

$$(P) = \frac{T_P}{T_{I^-}}\left(\frac{(I^-)}{(\Delta\omega_{max})^2D_{max}}\right)_{I^-}((\Delta\omega_{max})^2D_{max})_P \qquad (10)$$

The subscripts in the foregoing equation show whether the indicated terms refer to the standard iodide solution ($I^-$) or the periodate solution (P).

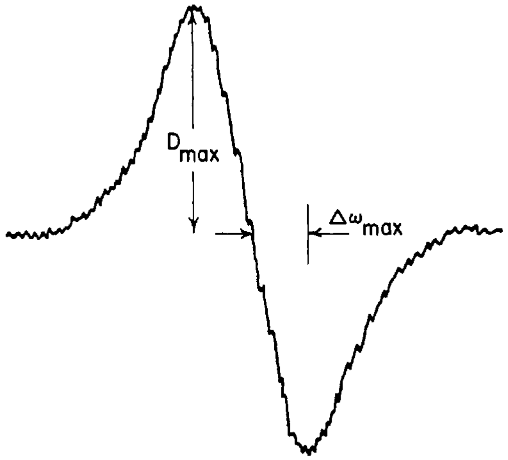

Figure 1.—Derivative curve for nmr absorption mode.

**Results and Discussion.**—The recorded nmr spectra from the periodate solutions covered only 20 G, and the observed spectra showed $\Delta\omega_{max}$ equivalent to only 1 G (see Table I). A calculation utilizing eq 7 shows that the quadrupole coupling constant for $^{127}I$ in $H_4IO_6^-(aq)$ need be only 85 MHz or greater in order that the $^{127}I$ line be unobservable. In view of the large coupling constants known for iodine nuclei in other compounds,[16,17] exceeding this small value is very probable for $H_4IO_6^-(aq)$ or a monovalent periodate species such as $H_2IO_5^-(aq)$.

While the observed signal has been attributed by the authors to the tetrahedral metaperiodate, other explanations of the cause of this signal are possible. A brief consideration of these causes is in order. It is conceivable that the signal observed was due to an increase of the symmetry of the field around the central iodine to octahedral because of rapid proton exchange between $H_4IO_6^-(aq)$ and solvent water. In such a case, $q$ is zero, and the resonance signal is unbroadened. Solutions of pure $H_5IO_6$ in water were studied and no $^{127}I$ resonance was found, which indicates that proton exchange between un-ionized acid and solvent does not increase the symmetry of $H_5IO_6(aq)$ to octahedral. Similarly, since proton exchange between $H_4IO_6^-(aq)$ and solvent should proceed through the $H_5IO_6$ structure, an effectively octahedral field in the $H_4IO_6^-(aq)$ ion is ruled out. Furthermore, the mean lifetime of protons of $H_4IO_6^-(aq)$ would need to be less than $10^{-11}$ sec which seems excessively short.

It is also remotely possible that the observed signal might have been that due to the average of two signals from rapidly exchanging $IO_4^-(aq)$ and $H_4IO_6^-(aq)$.

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[12] A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961, p 314.

[13] W. Gordy, W. V. Smith, and R. F. Trambarulo, "Microwave Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1953, p 256.

[14] Z. Luz and I. Pecht, *J. Am. Chem. Soc.*, **88**, 1152 (1966).

[15] R. M. Kren, "A Study of Periodate Equilibria in Aqueous Solution," Ph.D. Thesis, Washington State University, 1967, p 26 ff.

[16] R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1965, p 322.

[17] T. P. Das and E. L. Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Academic Press Inc., New York, N. Y., 1958.

TABLE I

DATA FOR COMPUTATION OF $K_d^0$ AND VALUES OBTAINED FOR $K_d^0$ [a]

| $T_{IO_4^-}$, °C | $(\Delta\omega_{max})_{IO_4^-}$, cm | $(D_{max})_{IO_4^-}$, cm | $\left[\frac{10^4 C_{I^-}}{(T_{I^-})(\Delta\omega_{max})^2(D_{max})}\right]_{I^-}$, $M$ cm$^{-3}$ deg$^{-1}$ | Av $K_d^0$ |
|---|---|---|---|---|
| 2 | 1.07[b] | 4.65 | 2.24 | 3.4 |
| | 1.03[b] | 5.30 | | |
| | 1.02[b] | 5.53 | | |
| | 1.01[b] | 5.28 | | |
| 3 | 0.97 | 5.28 | 1.64 | 5.1 |
| | 0.94 | 5.40 | 1.60 | |
| | 0.93 | 5.48 | 1.73 | |
| | 0.93 | 5.24 | 1.73 | |
| | 0.91 | 5.35 | 1.73 | |
| | 0.94 | 5.40 | 1.73 | |
| | 0.92 | 5.24 | 1.73 | |
| 4 | 0.98 | 4.72 | 1.90 | 4.2 |
| | 0.95 | 5.64 | 1.64 | |
| 5 | 0.89 | 5.98 | 1.64 | 4.6 |
| | 0.96 | 6.36 | 1.64 | |
| | 0.90 | 6.37 | 1.60 | |
| 6 | 0.89 | 6.93 | 1.64 | 4.4 |
| | 0.86 | 6.74 | 1.73 | |
| | 0.93 | 5.27 | 1.90 | |
| | 0.95 | 5.61 | 1.90 | |
| | 0.92 | 5.26 | 1.90 | |
| 7 | 0.85 | 7.66 | 1.60 | 5.5 |
| | 0.87 | 6.82 | 1.64 | |
| | 0.89 | 6.73 | 1.64 | |
| | 0.92 | 5.58 | 1.90 | |
| | 0.90 | 5.88 | 1.90 | |
| | 0.88 | 5.78 | 1.90 | |
| 8 | 0.85 | 5.80 | 1.90 | 5.9 |
| | 1.04[b] | 5.45 | 2.24 | |
| | 0.90 | 5.88 | 1.90 | |
| | 0.90 | 5.89 | 1.90 | |
| | 0.89 | 6.18 | 1.90 | |
| 11 | 0.84 | 6.78 | 1.90 | 7.7 |
| | 0.82 | 6.73 | 1.90 | |
| | 0.83 | 6.42 | 1.90 | |
| | 0.84 | 6.78 | 1.90 | |
| | 0.84 | 6.77 | 1.90 | |
| 12 | 0.84 | 6.92 | 1.90 | 11.0 |
| 13 | 0.93[b] | 6.78 | 2.24 | 9.7 |
| | 0.83 | 7.06 | 1.90 | |
| | 0.84 | 7.09 | 1.90 | |
| | 0.82 | 7.16 | 1.90 | |
| | 0.83 | 7.10 | 1.90 | |
| 15 | 0.91[b] | 7.58 | 2.24 | 12.0 |
| 16 | 0.89[b] | 7.80 | 2.24 | 12.0 |
| | 0.89[b] | 7.99 | 2.24 | |
| 18 | 0.87[b] | 8.12 | 2.24 | 17.0 |
| | 0.89[b] | 8.29 | 2.24 | |
| | 0.86[b] | 8.25 | 2.24 | |
| | 0.86[b] | 7.65 | 2.24 | |

[a] Total periodate concentration was 0.288 $M$ except where indicated; pH 5.0. [b] Total periodate concentration was 0.436 $M$.

This would be the state of affairs if the dehydration and hydration reactions shown in eq 1 were very rapid. Under these circumstances, one would expect the signal to be unobservable because of the large quadrupolar broadening expected in the $H_4IO_6^-$(aq) ion. If, however, the line was not broadened beyond observability, the width would be expected to be temperature dependent; this was not observed. Furthermore, the results of previous work[18] allow one to calculate that the exchange rate would be too slow if the $IO_4^-$(aq) and $H_4IO_6^-$(aq) resonances are separated by more than 10 ppm, a situation which is expected to exist. To eliminate this hypothesis experimentally, we have studied the nmr spectra of samples of $KIO_4$ and $NaIO_4$ dissolved in freshly distilled dimethyl sulfoxide and in N,N-dimethylformamide. Both of these solutions showed $^{127}I$ nmr signals at the same frequency and magnetic field strength as the aqueous periodate solutions, thus demonstrating that the periodate species in these nonaqueous solvents is the same one detected in our experiments in aqueous periodate solutions, *i.e.*, $IO_4^-$.

The conclusion which we have drawn from these

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(18) K. Kustin and E. C. Lieberman, *J. Phys. Chem.*, **68**, 3869 (1964).

considerations is that the signals observed in aqueous periodate solutions are due solely to the $IO_4^-$(aq) ion. The measured values of $D_{max}$, $\Delta\omega_{max}$, and $T$ for these solutions, along with the corresponding quantities for the signals observed from a standard iodide solution, are recorded in Table I. These data allow computation of the $IO_4^-$(aq) and $H_4IO_6^-$(aq) concentrations of the solutions and the values of $K_d^0$ which are also recorded in Table I. In these calculations, the activity of water was taken as equal to the mole fraction of water, approximately unity. A plot of ln $K_d^0$ *vs.* $(1/T) \times 10^3$ is shown in Figure 2. The line was obtained by the method of least squares, and from its slope, $\Delta H_d^0$ was evaluated to be 14.8 ± 1.1 kcal/mole. Values of $K_d^0$ for 25 and 40° were obtained by extrapolation of the plot in Figure 2, and, as seen from Table II, these values agree well with those reported previously.[4,5] It should be noted that only extrapolated values of $K_d^0$ can be obtained for the higher temperatures from the nmr study. This results from the fact that more than 95% of the periodate is in the form of $IO_4^-$(aq) at 25°, and beyond this percentage any increase in $IO_4^-$(aq) concentration is undetectable from nmr spectra. The present study finds a lower $K_d^0$ at 5° than did the previous ones, and since many more low-temperature data were taken in the present study, it is likely that the value presented here is the most reliable. At 25°, $\Delta G_d°$ was estimated to be −2.0 ± 0.1 kcal/mole and $\Delta S_d°$ was calculated to be 56 ± 4 eu.

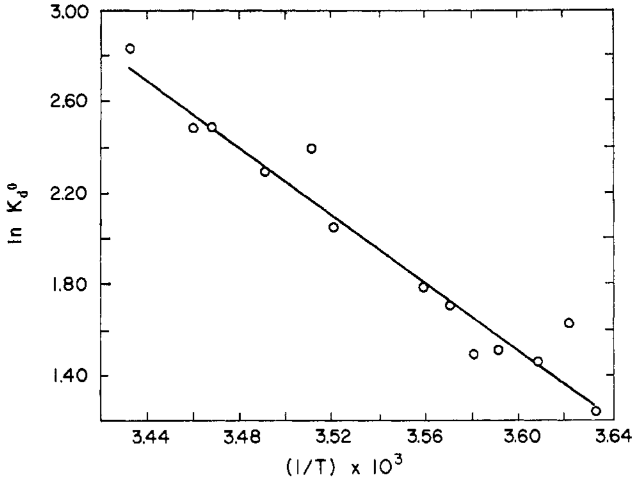

Figure 2.—Graph of ln $K_d^0$ *vs.* $(1/T) \times 10^3$ from the nmr data reported in this research.

Table II

Comparison of Reported Values of $K_d^0$

| Temp, °C | Ref 4 | Ref 5 | This study |
|---|---|---|---|
| 5 | *Ca.* 11 | 6.0 ± 0.2 | 4.7 ± 0.2 |
| 18 | *Ca.* 25 | *Ca.* 20 | 16 ± 1.1 |
| 25 | 40 | 43 ± 17 | 29 (extrap) ± 2 |
| 40 | *Ca.* 95 | 110 ± 30 | 94 (extrap) ± 7 |

## The Solubility Product of $CsIO_4$

Table III

A Comparison of Experimental and Calculated Solubilities of $CsIO_4$

| Temp, °C | pH | Solubility of total periodate, *M* Exptl | Solubility of total periodate, *M* Calcd |
|---|---|---|---|
| 5 | 1.33 | 0.0724 | 0.0731 |
| | 2.41 | 0.0327 | 0.0319 |
| | 3.38 | 0.0288 | 0.0284 |
| | 4.02 | 0.0288 | 0.0282 |
| | 4.16 | 0.0288 | 0.0282 |
| | 4.50 | 0.0286 | 0.0282 |
| 25 | 1.15 | 0.0951 | 0.0894 |
| | 2.12 | 0.0660 | 0.0675 |
| | 2.93 | 0.0644 | 0.0631 |
| | 3.36 | 0.0640 | 0.0625 |
| | 3.85 | 0.0635 | 0.0625 |
| | 4.37 | 0.0618 | 0.0625 |
| | 5.21 | 0.0635 | 0.0625 |
| | 5.89 | 0.0610 | 0.0625 |
| | 5.98 | 0.0631 | 0.0625 |
| 40 | 1.32 | 0.1335 | 0.136 |
| | 2.40 | 0.1122 | 0.111 |
| | 3.33 | 0.1100 | 0.109 |
| | 3.70 | 0.1105 | 0.109 |
| | 3.76 | 0.1104 | 0.109 |
| 60 | 4.0 | 0.2018 | |

In Table III are recorded the solubilities of $CsIO_4$ obtained for aqueous solutions of various pH values at three different temperatures. These data are most readily interpreted by use of eq 6 when it is rearranged to

$$(I_tf_1)^2 = \frac{K_{sp}^0}{K_d^0}\left(K_d^0 + 1 + \frac{K_2^0f_1}{f_2a_{H^+}}\right) + \frac{K_{sp}^0f_1a_{H^+}}{K_d^0K_1^0} \qquad (11)$$

It is obvious from the form of this equation that a plot of $I_t^2f_1^2$ *vs.* $f_1a_{H^+}$ will yield a straight line with intercept $K_{sp}^0(1 + (1/K_d^0))$ and slope $K_{sp}^0/K_d^0K_1^0$ for all pH values below 6 where the term $K_2^0f_1/f_2a_{H^+}$ is negligible compared with $(1 + K_d^0)$. Such plots are shown in Figure 3. The values of the intercept obtained and the values of $K_{sp}^0$ calculated therefrom are tabulated in Table IV. The values of $K_d^0$ employed are those reported from this study, and the values of $K_1^0$ (5°, $6.9 \times 10^{-4}$; 25°, $1 \times 10^{-3}$; 40°, $1.1 \times 10^{-3}$) are from a previous study.[5] The values for the activity

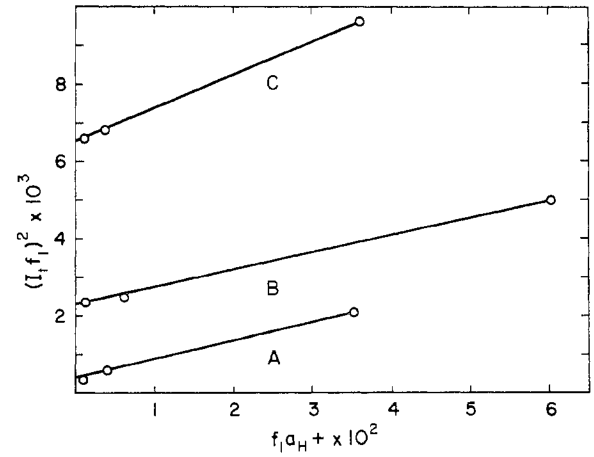

Figure 3.—Plot of $(I_tf_1)^2$ *vs.* $f_1a_{H^+}$ for $CsIO_4$ at (A) 5°, (B) 25°, and (C) 40°.

TABLE IV

$K_{sp}^0$ FOR $CsIO_4$

| Temp, °C | $K_{sp}^0$ |
|---|---|
| 5 | $(3.96 \pm 0.17) \times 10^{-4}$ |
| 25 | $(2.24 \pm 0.07) \times 10^{-3}$ |
| 40 | $(6.53 \pm 0.04) \times 10^{-3}$ |

coefficients $f_1$ and $f_2$ can be calculated from the Davies equation[19]

$$-\log f_i = Az_i^2[(\mu^{1/2}/(1 + \mu^{1/2})) - 0.3\mu] \qquad (12)$$

where $\mu$ is the ionic strength in moles per liter, $z_i$ is the charge on the $i$th type of ion, and $A$ is a constant for a given temperature in water.[20]

A graph was made of $-\log K_{sp}^0$ *vs.* $(1/T) \times 10^3$ which included a point for 60° calculated from a single determination of the solubility at that temperature. From this plot, $\Delta H_{soln}^\circ$ was calculated to be 13.1 kcal/mole. $\Delta G_{soln}^\circ$ at 25° was calculated to be 1.91 ± 0.05 kcal/mole, and $\Delta S_{soln}^\circ$ was calculated to be 37.6 eu.

Table III also indicates the solubilities calculated using the values of $K_{sp}^0$ found. It is seen that the values of $K_{sp}^0$ employed adequately explain the experimental data.

Solubility studies at higher pH values than those reported were not feasible because of the precipitation of periodates of the cation of the inert electrolyte. For example, when $NaNO_3$–$NaOH$ mixtures were used to obtain initial pH values in the range 10–13, a solid of high sodium content (probably $Na_2H_3IO_6$) separated from solution as a consequence of the higher concentration of doubly and triply charged periodate anions in the more basic solutions. After a literature search and several exploratory experiments, it was found that a suitable ionic medium could not be found to extend the pH range above about 6. Previous studies in basic solution[2,5] were either done at a single pH or employed periodates of such low solubilities that concentrations of the various periodate species were never high enough to cause precipitation of the cations added to maintain constant ionic strength.

In order to explain the formation of salts of the anion $H_2I_2O_{10}^{4-}$, a dimerization equilibrium has been postulated at high pH[21]

$$2H_3IO_6^{2-}(aq) \rightleftharpoons H_2I_2O_{10}^{4-}(aq) + 2H_2O(l)$$

$$K_{dim}^0 = \frac{(H_2I_2O_{10}^{4-})f_4a_{H_2O}^2}{(H_3IO_6^{2-})^2f_2^2} = 2400 \text{ at } 1.0°, 600 \text{ at } 25.0° \qquad (13)$$

This anion is probably present in the salt $Cs_4H_2I_2O_{10} \cdot 8H_2O$, which we have prepared and reported in the Experimental Section. The inclusion of this dimerization equilibrium in the calculations of the solubility of $CsIO_4$ is of no importance in evaluating $K_{sp}^0$ from the data obtained in this study, because even at the highest pH studied, the concentration of dimer in solution is not significant.

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[20] R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd ed, revised, Butterworths and Co. Ltd., London, 1965, p 468.

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# Thermodynamic Studies in the Polyiodide Systems $RbI$-$RbI_3$, $NH_4I$-$NH_4I_3$, $CsI$-$CsI_3$, and $CsI_3$-$CsI_4$

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The free energy of the reaction $MI(s) + I_2(s) = MI_3(s)$ for the polyiodide systems $RbI$–$RbI_3$, $NH_4I$–$NH_4I_3$, and $CsI$–$CsI_3$ and of the reaction $CsI_3(s) + {}^1/_2I_2(s) = CsI_4(s)$ was determined from emf measurements of solid-state cells of the types $Ag|AgI|C$, $MI$–$MI_3$ (or C, $CsI_3$–$CsI_4$) and $Ag|AgI|C$, $I_2(s)$. For the temperature range 25–113.5° $\Delta G^\circ$ values (kcal/mole) of the above reactions are given by $\Delta G^\circ = -2.48 + 2.30 \times 10^{-3}(T - 273)$ for $RbI$–$RbI_3$, $\Delta G^\circ = -1.78 + 1.10 \times 10^{-3}(T - 273)$ for $NH_4I$–$NH_4I_3$, $\Delta G^\circ = -3.48 + 0.92 \times 10^{-3}(T - 273)$ for $CsI$–$CsI_3$, and $\Delta G^\circ = -0.64 + 0.57 \times 10^{-3}(T - 273)$ for $CsI_3$–$CsI_4$. From these free energies and the vapor pressure of solid iodine, dissociation pressure expressions for the polyiodides were found for the same temperature range. The standard entropies, free energies, and heats of formation as well as the aqueous heats of solution of the polyiodides at 25° were calculated.

## Introduction

Although the existence of polyiodides of ammonium, as well as of the alkali metals cesium and rubidium, has long been known, the only thermodynamic measurements reported on these systems have been those of Foote, *et al.*,[1-3] and Stepin, Babkov, and Sas.[4] To obtain thermodynamic data for the reaction

$$MI_x(s) + yI_2(s) = MI_{x+2y}(s) \qquad (1)$$

an emf study was undertaken on cells of the types

$$Ag|AgI|C, MI_x\text{–}MI_{x+2y} \qquad (I)$$

$$Ag|AgI|C, I_2(s) \qquad (II)$$

where $MI_x$–$MI_{x+2y}$ represents the $NH_4I$–$NH_4I_3$, $RbI$–$RbI_3$, $CsI$–$CsI_3$, and $CsI_3$–$CsI_4$ systems and $I_2(s)$ elemental iodine.

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[2] H. W. Foote, W. M. Bradley, and M. Fleischer, *ibid.*, **37**, 21 (1933).

[3] H. W. Foote and M. Fleischer, *ibid.*, **44**, 633 (1940).

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