NOTES

Hydrolytic Behavior of Metal Ions. IV. The Acid Constant of Uranium(IV) as a Function of Temperature[1,2]

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Received February 24, 1955

In an earlier paper it was shown[3] that the initial hydrolysis of U(IV) at room temperature can be described by the equation

$$U^{+4} + H_2O \rightleftharpoons UOH^{+3} + H^+ \qquad (1)$$

with the equilibrium constant

$$k_{01} = \frac{m_{UOH^{+3}}\, m_{H^+}}{a_{H_2O}\, m_{U^{+4}}}\, G_{01} = \frac{k^m_{01}}{a_{H_2O}}\, G_{01} \qquad (2)$$

where m is the molarity, k^m_{01} the concentration quotient, G_{01} the appropriate activity coefficient quotient and a_{H_2O} the activity of water. The temperature coefficient of equilibrium (1) has now been investigated at an ionic strength $\mu = ca.\ 0.5$ by determining k^m_{01} at 10 and 43° using the same method by which k^m_{01} at 25° had been determined.

The experimental procedure was similar to the one described earlier, *i.e.*, spectrophotometric determination of the acid dependence of the prominent 648 mμ peak of U^{+4}. Aliquots of a U(IV) stock solution were mixed with $NaClO_4$–$HClO_4$ solutions of appropriate acidity and a supporting electrolyte concentration of 0.5 M at the temperature of interest. The solutions were then drained into jacketed (thermostated) 10 cm. absorption cell. Optical density readings were obtained with a Beckman Model DU quartz spectrophotometer. Readings were started as soon as possible after mixing, usually within one minute, and were continued long enough to permit extrapolation to zero time, the time of mixing. All work was carried out under nitrogen which was purified from oxygen with copper shavings at 500°.

Computations of the concentration of unhydrolyzed U^{+4} were made from the difference ΔE of the extinction coefficients at 648 mμ (E_{648}) and at 700 mμ (E_{700}) rather than from E_{648} alone since by use of such differences somewhat higher precision can be obtained. The extinction coefficient difference for unhydrolyzed U^{+4} ($\Delta E_{U^{+4}}$) at the various temperatures was obtained from the optical densities in 2 M $HClO_4$ with a minor correction for hydrolysis at this acidity. Although this technique involves successive approximations for the evaluation of $\Delta E_{U^{+4}}$ the method appeared preferable to determination of $\Delta E_{U^{+4}}$ at considerably higher acidities where hydrolysis becomes negligible, since the extinction coefficients at very high ionic strength cannot be considered independent of ionic strength. Values of 63.5 and 57 were obtained for $\Delta E_{U^{+4}}$ at 10 and 43°, respectively, which may be compared with the earlier value $\Delta E_{U^{+4}} = 59.5$ at 25°. For the hydrolysis product (UOH^{+3})$\Delta E = 5.0$ had earlier been found at 25° and this value was assumed constant over the temperature range studied.

The results of the experiments are summarized in Table I. The value of k^m_{01} increases rapidly with temperature from 0.0125 at 10° to 0.100 at 43°. From the earlier data a "best" value $k^m_{01} = .0342$ at 25° may be obtained for the same ionic strength. From these values of k^m_{01} an apparent heat and entropy change for reaction (1) of 11.2 kcal. and 31 e.u. (25°) can be computed. For evaluation of the standard enthalpy ($\Delta H°$) and entropy ($\Delta S°$) changes, knowledge of the variation of k_{01} with T is necessary. Since it had earlier been shown that at 25° a modified Debye–Hückel equation permits evaluation of k_{01} at 25°, similar extrapolation functions were used at 10 and 43°. Variations of the constants in this equation with temperature were taken into consideration,[4] and $\mathring{a}$, the average distance of closest approach, was considered independent of temperature. Values of k_{01} of 0.075, 0.21 and 0.66 at 10, 25 and 43°, respectively, were estimated. From the slope of the straight line plot of log k_{01} (Fig. 1) $\Delta H° = 11.7$ kcal. was obtained, which with the value of k_{01} at 25° yields $\Delta S° = 36$ e.u. for reaction (1). Combination of this value with $S^\circ_{H_2O} = 16.7$ e.u.[5] and $S^\circ_{U^{+4}} = -78$ e.u.[5] yields $S^\circ_{UOH^{+3}} = -25$ e.u., which is in good agreement with the estimate $S^\circ_{UOH^{+3}} = -30$ e.u. given in the Bureau of Standards tables.[5]

Table I

Acid Constant of Uranium(IV) in Perchlorate Solutions, $\mu = ca.\ 0.5$, 7.28×10^{-4} M U(IV)

10.0 ± 0.2°C.				43.0 ± 0.3°C.			
Final M H^+	$E_{648} - E_{700}$	% U^{+4}	k^m_1	Final M H^+	$E_{648} - E_{700}$	% U^{+4}	k^m_1
0.512	61.4	96.6	(0.018)	0.512	48.5	83.7	0.100
.512	62.4	98.2	(.009)	.309	43.9	74.9	.104
.1045	57.2	89.4	.0123	.2073	39.9	67.2	.101
.0440	50.6	78.0	.0124	.1561	37.2	62.0	.096
.0338	47.5	72.8	.0126	.1561	37.0	61.7	.097
.02379	43.0	65.0	.0128	.1045	32.0	52.0	.096
.01362	36.3	53.4	.0119	.0646	25.2	38.8	.102
.00866	28.4	39.9	.0130	.0443	20.5	29.7	.105
.00370	17.6	21.4	.0136		Average:		.100
.00189[a]	12.9	13.4	.0122				
	Average:		.0125				

[a] 3.64×10^{-4} M U(IV).

The rather large positive entropy change for the hydrolysis reaction is probably due to the fact that the hydrolysis product, an ion of charge plus 3, tends to orient water molecules considerably less strongly than the unhydrolyzed ion with charge plus 4. If as a first approximation we assume that this electrostatic effect on the entropy is equal to

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[1] This document is based on work performed for the U. S. Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] Previous paper: K. A. Kraus and R. W. Holmberg, *J. Phys. Chem.*, **58**, 325 (1954).

[3] K. A. Kraus and F. Nelson, This Journal, **72**, 3901 (1950).

[4] H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Second Edition, Reinhold Publishing Corp., New York, N. Y., 1950, p. 119.

[5] "Selected Values of Chemical Thermodynamic Properties," by F. D. Rossini, *et al.*, Circular of the National Bureau of Standards, 500 (1952).

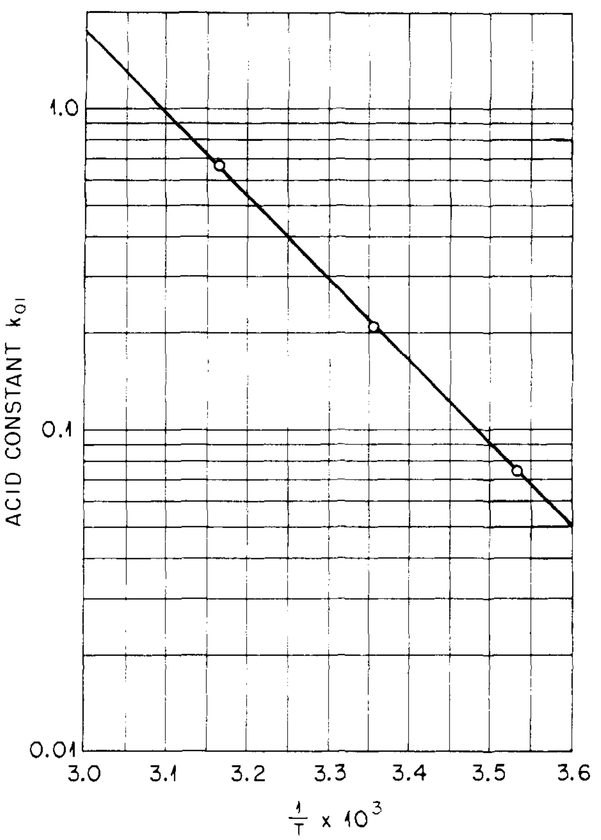

Fig. 1.—Temperature dependence of the U(IV) acid constant.

the entropy difference between U^{+4} and U^{+3} after correction for the entropy of hydrogen ($S^\circ_{U^{+3}}$ = −30 e.u., $S^\circ_{1/2H_2}$ = 15.6 e.u.[5]) the entropy change for reaction (1) readily can be accounted for.

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Studies on the Chemistry of Halogens and of Polyhalides. IV. On the Behavior of Iodine and of Iodine Halides in Acetonitrile[1,2]

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RECEIVED MARCH 28, 1955

Spectrophotometric investigations of the solutions of iodine monochloride[4] in acetonitrile have shown that this compound undergoes an ionic dissociation.

$$2ICl \rightleftharpoons I^+ + ICl_2^-$$

It was observed, however, that the absorption spectrum of iodine chloride in acetonitrile changed with time. The ultraviolet peak at 227 mμ which is due to the ICl_2^- ion[5] slowly increased in intensity, without, however, showing a quantitative conversion of iodine monochloride to the iododichloride ion[6] even after periods of several weeks.

Although it is well known that iodine monochloride and iodine bromide conduct electric current in certain solvents and in the molten state,[7] very little quantitative work has, as yet, been done either upon their conductances in dilute solutions or on the mechanism of such conductance. It was thought that such study may be of interest to the understanding of the behavior of interhalogen compounds in acetonitrile solutions.

Experimental Part

Conductance Measurements.—The conductivity bridge, and the measurement conditions were described in a previous communication.[2] The temperature was maintained at 25 ± 0.003°.

Spectrophotometric Measurements.—All spectrophotometric measurements were done on a Cary recording spectrophotometer model 11. Stoppered silica cells of path length 1.00 ± 0.01 cm. were used. Measurements were made at the room temperature of approximately 25°.

Solvents.—Acetonitrile obtained from the Matheson, Coleman and Bell Co. was purified by the method already described.[2] It is interesting to note that different batches of the solvent seemed to differ considerably in the amount of impurities present, and in some cases required several additional distillations over phosphorus pentoxide before solvent of sufficient purity was obtained.

Iodine.—C.P. iodine (J. T. Baker) was purified by sublimation from a mixture of calcium oxide and potassium iodide.

Iodine Monochloride.—Iodine monochloride was prepared by the method of Cornog and Karges.[8] It was repeatedly purified by fractional crystallization *in vacuo*. The melting point was 27.2° which is identical with the literature value.

Iodine Cyanide.—Iodine cyanide was prepared and purified by the method of Bak and Hillebert.[9] The melting point in a sealed tube was 146–147°, identical with the value reported.

Iodine Bromide.—Iodine bromide was prepared by the addition of 88 g. (0.55 mole) of bromine to 127 (0.50 mole) of iodine. The mixture was warmed on a water-bath until the iodine completely dissolved. When the mixture was cooled, solid iodine bromide crystallized out. The product was purified by repeatedly melting and cooling the crystals and discarding each time approximately 20% of the liquid melt. This procedure was repeated until the same melting point was obtained on two successive recrystallizations. The melting point was found to be 41.5° as compared with the value of 42° reported in the literature.[10]

Solutions.—Stock solutions were prepared by dissolving a weighed amount of the solute in purified acetonitrile. The exact concentrations were determined by iodometric titrations. Aliquots of stock solutions were then diluted to required concentration. All the solutions were at first prepared in a dry-box and the absorption cells and the conductance cells were likewise filled there. Since, as shall be described below, the absorption spectra as well as the specific conductance of the solutions showed a pronounced change with time, a special all-glass apparatus was designed which permitted the carrying out of the purification of the solvent, preparation of solutions at various known concentrations, and the measurement of the electrical conductance without any exposure to the atmosphere.[11]

Results

Iodine Monochloride.—Absorption spectra of iodine monochloride in acetonitrile have been re-

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(1) Abstracted in part from the Ph.D. thesis of Norman E. Skelly, State University of Iowa, 1955.

(2) Previous paper of this series, THIS JOURNAL, **76**, 5309 (1954).

(3) Du Pont Postgraduate Fellow, 1953–1954.

(4) R. E. Buckles and J. F. Mills, THIS JOURNAL, **76**, 4845 (1954).

(5) A. I. Popov and J. N. Jessup, *ibid.*, **74**, 6127 (1952).

(6) The ICl_2^- ion has often been called the dichloroiodide. However, since it is produced by the addition of the chloride ion to iodine monochloride it seems more correct to call it iododichloride.

(7) (a) L. Bruner and A. Galecki, *Z. physik. Chem.*, **84**, 513 (1913); (b) N. N. Greenwood and H. J. Emeleus, *J. Chem. Soc.*, 987 (1950).

(8) J. Cornog and R. A. Karges, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 165.

(9) B. Bak and A. Hillebert, *Org. Syntheses*, **32**, 29 (1952).

(10) A. E. Gillam, *Trans. Faraday Soc.*, **29**, 1132 (1933).

(11) A. I. Popov, N. E. Skelly and R. Rygg, to be published.