[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

Extraction of Uranyl Ion from Some Aqueous Salt Solutions with 2-Thenoyltrifluoroacetone

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The extraction of uranyl ion from aqueous solutions of sodium perchlorate, chloride, nitrate, sulfate and fluoride with benzene solutions of 2-thenoyltrifluoroacetone has been studied. Values of stability constants for complexing of uranyl by the anions of the above salts were evaluated at ionic strength 2.00 at 10, 25 and 40°. The extraction from solutions of varying molarities of perchlorate, chloride and nitrate was also studied at 25°. The extent of complexing by fluoride was measured at several values of the ionic strength to obtain an estimate of the activity constant.

The stability constants for complexes of uranyl with a number of anions have been reported in the literature. Ahrland[1] has reported values for monochloroacetate, thiocyanate, acetate, sulfate, chloride bromide, nitrate and glycolate. He has employed potentiometric and spectrophotometric methods, usually at 20° and ionic strength of 1.00. Nelson and Kraus[2] estimated the constant for the uranyl chloride complex from their studies of the U(IV)-(V)(VI) system. Betts and Michels[3] studied the uranyl nitrate and uranyl sulfate systems spectrophotometrically at 25° and ionic strength 5.38 and 2.65, respectively. These various results show conclusively that the complex ions of uranyl with chloride and nitrate are quite weak. The complex with sulfate is much stronger, while that with fluoride has not been reported in the literature. A value of about 20 for the fluoride complex constant has been estimated from ion-exchange data, however.[4]

The purpose of the present work was to study the extraction of uranyl ion from aqueous solutions of various sodium salts, particularly perchlorate, chloride, nitrate, sulfate and fluoride with benzene solutions of 2-thenoyltrifluoroacetone (TTA). Stability constants can be calculated from such data, as has been reported for various other systems.[5-9] It was of interest to compare the results obtained by this method with those found by other techniques. It also was desired to study the extraction at different temperature in order to obtain thermodynamic data. Since chloride and nitrate form such weak complexes and the effect might be attributed to variations in activity coefficients, it was desired to study the extraction from solutions of varying molarity of these anions. The uranyl fluoride system was studied at several values of the ionic strength to allow an estimation of the activity constant for complex formation at 25°.

The calculations involved in evaluating stability constants of complex ions from such solvent extraction data have been amply covered elsewhere.[6] The final equation used here for the divalent uranyl ion is

$$\frac{R^{a}{}_{b}}{R_0} = 1 + k_{01}\frac{(\mathrm{HX})}{(\mathrm{H}^+)} + k_{02}\frac{(\mathrm{HX})^2}{(\mathrm{H}^+)^2} \qquad (1)$$

where $R^{a}{}_{b}$ is the distribution ratio, aqueous to benzene, in the presence of the complexing molecule, HX; R_0 is the same ratio in the absence of complexing agent. For strong acids the term $(\mathrm{HX})/(\mathrm{H}^+)$ is replaced by the concentration of the anion, (X^-). The equilibrium constants, k_{01} and k_{02}, are for the formation of the first and second complexes by the reactions

$$\mathrm{UO_2}^{++} + \mathrm{HX} = \mathrm{UO_2X}^+ + \mathrm{H}^+ \qquad (2)$$

$$\mathrm{UO_2}^{++} + 2\mathrm{HX} = \mathrm{UO_2X_2} + 2\mathrm{H}^+ \qquad (3)$$

The anion concentration is again substituted for the acid where the acid is strong. By plotting $R^{a}{}_{b}$ against $(\mathrm{HX})/(\mathrm{H}^+)$ (or against (X^-)) the values of k_{01} and k_{02} can be obtained easily. The method of least squares was used to fit the data and evaluate the constants.

Experimental

Materials and Apparatus.—The TTA was obtained from the Dow Chemical Co. It was found to be very light yellow in color and homogeneous in appearance. Its melting point was 43.0–43.5° and the molar absorbancy index in benzene at 330 mμ was 11,500. This compares favorably with the data reported by King and Reas.[10] No further purification of the TTA was attempted. It was always stored in the dark over phosphorus pentoxide.

C.P. grade chemicals were used throughout. All volumetric apparatus was calibrated. Sodium perchlorate was prepared by neutralizing standard perchloric acid with solid sodium hydroxide. The solution was heated, filtered to remove ferric hydroxide, and diluted to volume.

Uranium 233, used as the tracer, was obtained from the Oak Ridge National Laboratory. It was purified of possible alpha emitting decay products by TTA extraction. The alpha counter was a methane-flow type used with a Nuclear Instrument and Chemical Corp. Model 162 scaler.

Procedure.—In order to find suitable acid and TTA concentrations to be used, a number of initial runs were made in perchlorate media. A TTA concentration of 0.50 *M* and hydrogen ion concentration of 0.050 *M* were selected as convenient values of these variables. Under these conditions at 25° and ionic strength 2.00, the constant for the reaction

$$\mathrm{UO_2}^{++}{}_{a} - 2\mathrm{HT_b} = \mathrm{UO_2T_{2b}} + 2\mathrm{H}^{+}{}_{a} \qquad (4)$$

was found to be 1.00×10^{-2}. The extraction was found to be dependent upon the square of both TTA and hydrogen ion concentrations.

For complexing studies the aqueous phase contained 0.05 *M* $\mathrm{HClO_4}$, the desired concentration of complexing agent, and sufficient $\mathrm{NaClO_4}$ to obtain the desired ionic strength. The benzene phase contained 0.50 *M* TTA and the U-233

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(1) (a) S. Ahrland, *Acta Chem. Scand.*, **3**, 783 (1949); (b) **3**, 1067 (1949); (c) **5**, 199 (1951); (d) **5**, 1151 (1951); (e) **5**, 1271 (1951); (f) **7**, 485 (1953).

(2) F. Nelson and K. A. Kraus, THIS JOURNAL, **73**, 2157 (1951).

(3) R. H. Betts and R. K. Michels, *J. Chem. Soc.*, Supp. issue, No. S286 (1949).

(4) K. A. Kraus, private communication.

(5) R. E. Connick and W. H. McVey, THIS JOURNAL, **71**, 3182 (1949).

(6) R. A. Day, Jr., and R. W. Stoughton, *ibid.*, **72**, 5662 (1950).

(7) E. L. Zebroski, H. W. Alter and F. K. Heumann, *ibid.*, **73**, 5646 (1951).

(8) W. C. Waggener and R. W. Stoughton, *J. Phys. Chem.*, **56**, 1 (1952).

(9) R. H. Betts and R. M. Leigh, *Can. J. Research*, **B28**, 514 (1950).

(10) E. L. King and W. H. Reas, THIS JOURNAL, **73**, 1806 (1951).

tracer at a concentration of about 10^{-5} *M*. The TTA had been previously hydrated by shaking with dilute $HClO_4$ overnight. An excess of 2.5% of TTA was added in order to accommodate a decrease in the total concentration of chelating agent due to aqueous phase solubility.

Equal volumes (5.00 ml.) of aqueous and benzene phases were then placed in 15-ml. glass-stoppered centrifuge tubes and shaken end-over-end in a constant temperature bath for two hours. This time was found more than ample for equilibration. Four tubes were normally prepared. At the end of the shaking period, the tubes were centrifuged and duplicate 0.5-ml. aliquots were taken for counting from the benzene phase of each tube. The aqueous phase could not be counted directly because of the large salt content. Therefore, a 1.00-ml. aliquot of this phase was withdrawn, diluted ten-fold with water and back-extracted for two hours with 2.00 ml. of 0.50 *M* TTA. Duplicate aliquots of the benzene phase were then taken for counting. The original benzene solution was counted to achieve a material balance. One-inch stainless steel plates were used for mounting the samples. The average precision attained in distribution ratios was usually better than ±5%. Material balances were normally better than 90%.

In order to compensate for the expansion or contraction of the benzene phase in runs at 10 and 40°, the tubes, after centrifuging, were allowed to come to 25° in a constant temperature bath before aliquots were taken for counting. This means, of course, that the distribution ratios reported at 10 and 40° are not those that actually exist at those temperatures. This does not affect the value of the complexing constant, however, as calculated from equation 1. No change in the distribution ratio was found to occur during the short time the tubes were allowed to stand in the bath.

Aqueous Complexing of Uranyl by TTA.—The possibility that the aqueous reaction

$$UO_2^{++} + HT = UO_2T^+ + H^+$$

might occur to a sufficient extent to necessitate a correction of the experimental data was investigated. This study was made by comparing the distribution of TTA between benzene and water in the presence and absence of uranyl ion. With shaking times up to six hours, the above reaction was found to occur only slightly. Either the extent of complexing is small or a much longer time is required to reach equilibrium. Therefore, no corrections for this complexing have been applied.

Results and Discussion

The distribution ratios obtained are listed in Tables I, II and III. The values of complexing constants calculated from these results are given in Table IV and thermodynamic data in Table V. The uncertainty in the values of the constants is at least ±10%. The constants are, of course, concentration, not activity constants, and hence contain as factors the activity coefficients of the various species involved. In the case of complexing by chloride and nitrate, the medium changes from 1.95 *M* sodium perchlorate to 1.95 *M* sodium chloride or nitrate, and the small complexing effect found here might actually be caused by variation in activity coefficients with the change in medium. The magnitude of the effect is approximately the same as that previously found by other methods.[1e,2,3] Betts and Michels[3] claim definite evidence for the existence of the species $UO_2NO_3^+$, from their results by the method of continuous variations. Such a question cannot be resolved, of course, without knowledge of the variations in activity coefficients at constant ionic strength. This question has been fully discussed recently by Young and Jones.[11] No thermodynamic data have been listed for the nitrate complex in Table V, since the data are of doubtful significance.

TABLE I

DISTRIBUTION RATIO, $R^a{}_b$, AS A FUNCTION OF COMPLEXING AGENT CONCENTRATION AT IONIC STRENGTH 2.00

Comp. agent, *M*	Chloride 10°	Chloride 25°	Chloride 40°	Nitrate 10°	Nitrate 25°	Nitrate 40°
0.00	0.80	1.00	0.97	0.80	1.00	0.97
.50	.95	1.36	1.43	.91	1.11	1.02
.75	..	..	1.85	..	..	..
1.00	1.12	1.88	2.03	1.02	1.24	1.07
1.50	1.35	2.22	2.50	1.12	1.34	1.16
1.75	..	2.44	..	..	..	1.23
1.95	1.65	2.71	3.10	1.25	1.46	1.29

Added NaF $\times 10_3$, *M*	Fluoride 10°	Fluoride 25°	Fluoride 40°	Added Na_2SO_4, *M*	Sulfate 10°	Sulfate 25°	Sulfate 40°
0.00	0.80	1.00	0.97	0.00	0.80	1.00	0.97
.50	..	1.39	..	.01	1.30	1.36	1.39
1.00	1.14	1.45	1.27	.03	2.26	2.74	2.50
2.00	1.71	1.62	1.73	.05	3.38	4.30	3.83
3.00	2.40	2.20	2.17	.07	5.04	6.09	7.25
4.00	3.03	2.51	2.59	.09	6.92	9.08	8.83
5.00	3.46	3.14	3.16	.11	..	11.80	..
6.00	4.08	3.53	3.60				
7.00	4.95	3.94	3.79				
8.00	6.00	4.62	4.08				
9.00	6.53	5.52	4.49				
10.00	7.50	5.95	..				

TABLE II

DISTRIBUTION RATIO, R'_b, AS A FUNCTION OF SODIUM FLUORIDE CONCENTRATION IN SOLUTIONS OF VARYING IONIC STRENGTH AT 25°

Added NaF $\times 10^3$, *M*	μ = 0.05	0.25	0.50	1.00
0.00	0.95	1.42	1.34	1.16
.50	1.52	...	..	..
1.00	2.08	2.20	2.01	2.29
2.00	3.07	3.39	2.86	2.99
3.00	4.28	4.36	4.01	4.13
4.00	5.79	5.52	4.95	4.71
5.00	6.63	6.14	5.83	5.56
6.00	7.60	7.54	6.81	5.79
7.00	8.72	8.75	7.23	7.00
8.00	9.40	9.58	7.65	7.43
9.00	...	10.63	8.39	8.57
10.00	11.69	...	9.00	..

TABLE III

DISTRIBUTION RATIO, $R^a{}_b$, AS A FUNCTION OF SALT CONCENTRATION AT 25°

Salt + acid,[a] *M*	$NaClO_4$	NaCl	$NaNO_3$
0.05	0.95	1.10	0.97
1.00	1.16	2.43	1.44
2.00	1.00	3.00	1.47
3.00	0.81	4.56	1.47
4.00	.72	6.09	1.45
4.50	..	11.6	..
5.00	.51	14.4	1.46
6.00	.45	...	1.50
7.00	..	...	1.47

[a] All solutions 0.05 *M* in $HClO_4$, HCl or HNO_3.

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[11] T. F. Young and A. C. Jones, "Annual Review of Physical Chemistry," Vol. 3, Annual Reviews, Inc., Stanford, Calif., 1952, p. 286.

TABLE IV

SUMMARY OF CONSTANTS

Reaction μ = 2.00	10°	25°	40°	
$UO_2{}^{++} + Cl^- = UO_2Cl^+$	0.58	0.88	1.14	
$UO_2{}^{+} + NO_3{}^- = UO_2NO_3{}^+$	0.30	0.24	0.17	
$UO_2{}^{++} + SO_4 = UO_2SO_4$	63	76	96	
$UO_2{}^{++} + 2SO_4 = UO_2(SO_4)_2{}^{=}$	5.8×10^2	7.1×10^2	8.2×10^2	
$UO_2\ {}^{+} + HSO_4{}^- = UO_2SO_4 + H^+$	6.1	6.4	6.5	
$UO_2{}^{++} + HF = UO_2F^+ + H^+$	55	26	21	
25°, μ =	0.05	0.25	0.50	1.00
$UO_2{}^{++} + HF = UO_2F + H$	51	37	24	27

TABLE V

FREE ENERGY, HEAT CONTENT AND ENTROPY CHANGES AT 25°, IONIC STRENGTH 2.00, FOR THE REACTIONS: $UO_2{}^{++} + nX^- = UO_2X_n{}^{+2-n}$

Complex formed	ΔF, kcal./mole	ΔH, kcal./mole	ΔS, kcal./deg./mole
UO_2Cl^+	0.08	3.8	12
UO_2SO_4	−2.6	2.3	16
$UO_2(SO_4)_2{}^{=}$	−3.8	1.4	18
UO_2F^+	−1.9	−5.4	−12

The constants for sulfate complexing are in general agreement with values measured by other methods.[1d,3] The distribution ratios listed in Table I have been corrected for change in hydrogen ion concentration by formation of bisulfate ion. A value of 0.084 for the ionization constant of bisulfate at 25° and ionic strength 2.00 was used in these calculations.[7] At 10° and 40° the values of the ionization constant used were 0.097 and 0.068, respectively. These were estimated from data for the variation of the constant with temperature at low ionic strength.[12] The extraction data indicate the formation of at least two sulfate complexes, in agreement with the results of Ahrland.[1d] Betts and Michels[3] did not report a second complex in their studies.

The extent of complexing of uranyl by fluoride found here is of the same magnitude as that estimated from ion-exchange data.[4] There was no indication of the formation of a second fluoride complex at the concentrations of fluoride employed. The distribution ratios in Table I have been corrected for change in hydrogen ion concentration by formation of hydrogen fluoride. It was assumed that ionization of hydrogen fluoride was negligible, the ionization constant being 6.71×10^{-4} at 25°.[13] An approximate value for the activity constant was obtained assuming the Debye–Hückel equation holds up to an ionic strength of 2.00. A plot of log k_{01} *versus* $\mu^{1/2}/(1 + 1.972\ \mu^{1/2})$ gave a value of about 60 on extrapolation to zero ionic strength. Kraus and Nelson[2] used this equation for estimation of the activity constant for formation of the uranyl chloride complex.

The distribution ratios obtained with salt solutions of different concentrations are given in Table III. In perchlorate media the ratio first increases somewhat, and then gradually decreases as the salt concentration is increased. In chloride media the ratio increases steadily as the salt concentration is increased, the increase being somewhat more rapid at about 4.5 *M* chloride. In nitrate media the ratio rises to 1.44 at 1.00 *M* nitrate and then remains essentially constant up to 7.00 *M* nitrate. The distribution ratios in all three media approach the same value as the concentration is decreased to 0.05 *M*.

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[12] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1943, p. 430.

[13] H. H. Broene and T. De Vries, THIS JOURNAL, **69**, 1644 (1947).

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Reactions of Silane with Unsaturated Hydrocarbons

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The reactions of silane with ethylene, acetylene and vinylsilane have been investigated in a system which circulated the gaseous reactants continuously through the reaction zone. Ethylene and silane at 450–510° produced ethylsilane, diethylsilane and smaller quantities of disilane, trisilane and a compound believed to be ethyldisilane. Acetylene and silane at 460–510° gave a small amount of vinylsilane, but the bulk of the product consisted of ethynylsilane, particularly ethynyldivinylsilane. With photochemical activation, the principal products were ethylsilane, *n*-butylsilane and 1,4-disilylbutane from silane and ethylene, and vinylsilane from silane and acetylene. Irradiation of a mixture of silane and vinylsilane under similar conditions gave 1,2-disilylethane, but at the same time a large amount of the vinylsilane polymerized to form a white solid. This solid was also produced, along with a volatile dimer, when vinylsilane alone was irradiated. Free-radical mechanisms are suggested for these reactions and are supported by the relative proportions of products.

Introduction

Recent studies have shown the alkylsilanes are formed when silane is heated with an olefin. The addition proceeds at moderate temperature when the reactants are under pressure; for example, Hurd[2] obtained ethyl-, diethyl- and triethylsilane by heating silane and ethylene to 100° under pressure. The reaction with ethylene at atmospheric pressure has been described by Fritz,[3] who allowed a mixture of silane and ethylene to react at 450° in a static system for 80 minutes. Ethyl-, diethyl-

[1] Abstracted from a thesis presented by David G. White to the Faculty of Arts and Sciences of Harvard University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] D. T. Hurd, U. S. Patent 2,537,763 (1951).

[3] G. Fritz, *Z. Naturforsch.*, **7b**, 207 (1952).