The possibility that Ru(IV) is reacting in appreciable concentrations to form $[Ru(bipy)_2H_2O)_2]^{+++}$ seems unlikely due to its known slow rate of reduction and the lack of any evidence for additional complexes which might be expected. In addition, test calculations of the molar ratio and continuous variation studies assuming that Ru(IV) is reacting alone or in combination with Ru(III) give meaningless results. However, it would be expected that quantitative studies of the formation of $[Ru(bipy)_3]^{++}$ could not be justified in the same manner due to the reduction step involved and the much longer periods of heating required.

Comparison to the Iron System.—The reaction between Fe(III) and 2,2′-bipyridine to give $(Fe(bipy)_3]^{++}$ differs from the analogous reaction with Ru(III) in that the Fe(III) reaction gives no indication of the formation of intermediates. Simon and Haufe[16] state that there is no reaction between Fe(III) and 2,2′-bipyridine in aqueous media, but rather that the reaction is

$$Fe^{+++} \rightleftharpoons Fe^{++} \rightleftharpoons [Fe(bipy)_3]^{++}$$

However, there is the possibility that the Fe(III) complexes do form, but that successive complexes form at a rate such that their presence has not been detected.

Considering the complexes individually, each metal, when in the bivalent state, forms a complex of great stability. The tervalent 3:1 complexes of both have been prepared by oxidation of the bivalent forms and are strong oxidizing agents. Although Ru(II), Ru(III) and Ru(IV) all apparently form bis complexes with 2,2′-bipyridine, there is no reliable evidence for the existence of analogous iron complexes in solution. Mono-2,2′-bipyridine complexes of Fe(II)[17] and Fe(III)[18] have been characterized. The present investigation is the first presentation of evidence for the $[Ru(bipy)]^{+++}$ complex. The ruthenium complexes demonstrate the necessity of considering elevated temperatures when seeking evidence of complex formation.

Dwyer[19] has recently prepared solid $[Fe(bipy)_2Cl_2]$, $[Fe(bipy)Cl_2]$ and $[Fe(phen)_2Cl_2]$ by removal of the organic base from the corresponding tris complexes at elevated temperatures *in vacuo*. Dissolution of these solids gave only the tris complexes, however.

The rates of reaction of Ru(II) and Fe(II) differ quite markedly from those of the corresponding tervalent ions. The Fe(II) reaction is essentially instantaneous. Qualitative data indicate that the Ru(II) reaction is considerably faster than the corresponding Ru(III) reaction, but still much slower than that of Fe(II).

In summary, it can be said that these two Group VIII metals are quite different in their reactions with 2,2′-bipyridine. A study of the osmium system would be of interest since osmium would be expected to be qualitatively more similar to ruthenium than to iron.

Acknowledgment.—The authors wish to express their appreciation for the financial support given to the project by the Atomic Energy Commission and for the helpful suggestions of Professor Francis P. Dwyer of the University of Sydney.

(16) A. Simon and W. Haufe, *Z. anorg. allgem. Chem.*, **230**, 160 (1951).

(17) J. Baxendale and P. George, *Trans. Faraday Soc.*, **46**, 55 (1950).

(18) W. B. Howsmon and W. W. Brandt, THIS JOURNAL, **76**, 6319 (1954).

(19) F. P. Dwyer and F. Basolo, *ibid.*, **76**, 1454 (1954).

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

Stability of Complexes of Uranium(IV) with Chloride, Sulfate and Thiocyanate

BY R. A. DAY, JR., R. N. WILHITE AND F. D. HAMILTON

RECEIVED JANUARY 17, 1955

Values of stability constants of complexes of uranium(IV) with chloride, sulfate and thiocyanate have been determined at ionic strength 2.0 at 10, 25 and 40°. The solvent extraction method, using 2-thenoyltrifluoroacetone as a chelating agent, was employed. Values for the changes in free energy, heat content and entropy at 25° are reported.

A quantitative study of the extraction of tetravalent uranium into benzene by the action of the organic chelating agent 2-thenoyltrifluoroacetone (TTA) has been reported by Betts and Leigh.[1] It was found that uranium (IV) was extracted into benzene as a neutral molecule containing four chelate groups per metal atom. Betts and Leigh also studied the extraction from aqueous solutions of sulfuric acid and found the existence of at least two complex species, $U(SO_4)^{++}$ and $U(SO_4)_2$. They reported values of the stability constants of these complexes but their method of calculation was questioned by Sullivan and Hindman[2] who recalculated their results by several methods. Ahrland and Larsson[3] reported stability constants of uranium(IV) with chloride and thiocyanate at 20° and ionic strength 1.00. They employed a potentiometric method for their measurements.

The purpose of the present work was to study the stability of some uranium(IV) complexes at dif-

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

(2) J. C. Sullivan and J. C. Hindman, THIS JOURNAL, **74**, 609 (1952).

(3) S. Ahrland and R. Larsson, *Acta Chem. Scand.*, **8**, 137 (1954).

TABLE I

DISTRIBUTION RATIO, R^a_b COR., AS A FUNCTION OF COMPLEXING AGENT CONCENTRATON AT IONIC STRENGTH 2.0

Comp. agent, *M*	Chloride			Comp. agent, *M*	Thiocyanate			Comp. agent, *M*	Sulfate		
	10°	25°	40°		10°	25°	40°		10°	25°	40°
0.00	0.42	0.48	0.25	0.00	0.42	0.48	1.25	0.00	0.42	0.48	1.25
0.50	1.38	.90	2.23	.05	2.00	1.55	2.84	.020	5.06	4.62	9.73
1.00	1.94	1.61	3.16	.10	3.38	2.47	4.81	.026	...	6.75	....
1.30	2.58	2.16	4.15	.15	6.10	3.73	7.67	.040	11.84	11.27	21.74
1.70	3.17	3.12	6.17	.20	9.08	5.79	10.78	.052	...	15.21	....
2.00	3.63	3.75	7.68	.25	11.74	8.45	14.80	.060	23.29	...	39.13
				.30	...	11.06	...	.080	37.89	33.64	64.64
								.100	55.07	50.08	102.2

ferent temperatures. The solvent extraction method employing TTA has been previously used for such purposes.[4] The complexing anions chosen for study were bisulfate, chloride, thiocyanate and fluoride. It was of interest to compare the results with those of Betts and Leigh and with those of Ahrland obtained by the potentiometric method. It was found that fluoride formed such a stable complex with uranium(IV) that only an estimate could be obtained of the constants by the method employed.

Experimental

Materials and Apparatus.—C.P. grade chemicals were used throughout. The TTA and sodium perchlorate, as well as the counting apparatus, were the same as previously reported.[4]

Uranium(IV) perchlorate, in macro concentration, was prepared by electrolytic reduction of uranyl perchlorate in a two-compartment cell. Tracer uranium 233 was reduced separately and then extracted into benzene–TTA for storage (see below).

Procedure.—Several attempts were made to employ only tracer uranium as in previous studies.[4] However, practically complete oxidation of uranium(IV) to uranyl ion occurred during the extraction. Solutions were deaerated and an atmosphere of nitrogen was used in the tubes but still considerable oxidation occurred. For this reason macro concentrations of uranium(IV), ranging from 0.0016 to 0.0037 *M*, were employed. No difficulty from oxidation was encountered at these concentrations.

Preliminary experiments in the absence of complexing agents gave a value of 0.48 for the distribution ratio, aqueous to benzene, in 1.00 *M* perchloric acid, $\mu = 2.0$, and using 0.0500 *M* TTA at 25°. From these data the concentration constant for the extraction reaction

$$U^{+4} + 4HT = UT_4 + 4H^+$$

was calculated as 3.3×10^5. From some of the data of Betts and Leigh[1] a value of about 4.5×10^5 can be calculated.

For complexing studies the aqueous phase was 1.040 to 1.080 *M* in perchloric acid. At this acidity hydrolysis of uranium(IV) is quite small.[5] In the chloride runs hydrochloric acid was substituted for perchloric acid. The concentration of uranium(IV) in the aqueous phase was determined before each run by measurement of the absorbance of the solution at 650 mμ, using a Beckman Model DU Spectrophotometer. The desired concentration of complexing agent was added and the ionic strength adjusted to 2.0 by addition of sodium perchlorate. The benzene phase was normally 0.0500 *M* in TTA. In some runs with higher concentrations of strong complexing agents, it was necessary to use 0.0750 *M* solutions. The TTA was hydrated as previously reported[4] and tracer uranium 233 was extracted into the TTA solution.

Equal volumes (5.00 ml.) of aqueous and benzene phases were then placed in 15-ml. glass-stoppered centrifuge tubes. Nitrogen was swept through the tubes to displace air and minimize oxidation during the extraction. The remainder of the procedure was the same as previously reported[4] except for two points. It was found that equilibrium was reached within 15 to 30 minutes, so the tubes were shaken only 30 minutes. Also the aqueous phase was not diluted before back-extraction because hydrolysis of uranium(IV) would occur. A 2.00-ml. aliquot of the aqueous phase was back-extracted with 0.500 *M* TTA directly, air in the tubes again being displaced by nitrogen. The average precision attained in the distribution ratios was usually better than ±5%. Material balances were normally better than 90%.

Results and Discussion

The distribution ratios obtained are listed in Table I. All values of R^a_b cor. refer to the distribution ratio, aqueous to benzene, corrected to equilibrium concentrations of 1.000 *M* hydrogen ion and 0.0500 *M* TTA. In making these corrections account was taken of the decrease in TTA and increase in hydrogen ion concentrations during extraction. The complexing constants calculated from these data are listed in Table II and the changes in free energy, heat content and entropy at 25° are given in Table III.

TABLE II

SUMMARY OF CONSTANTS

Reaction $\mu = 2.0$	10°	25°	40°
$U^{+4} + Cl^- = UCl^{+3}$	3.3	1.21	0.91
$U^{+4} + 2Cl^- = UCl_2^{+2}$	..	1.14	0.80
$U^{+4} + SCN^- = USCN^{+3}$	60	31	20
$U^{+4} + 2SCN^- = U(SCN)_2^{+2}$	2.0×10^2	1.3×10^2	95
$U^{+4} + HSO_4^- = USO_4^{+2} + H^+$	4.3×10^2	3.3×10^2	2.4×10^2
$U^{+4} + 2HSO_4^- = U(SO_4)_2 + 2H^+$	9.3×10^3	7.4×10^3	5.7×10^3

TABLE III

FREE ENERGY, HEAT CONTENT AND ENTROPY CHANGES AT 25°, IONIC STRENGTH 2.0, FOR THE REACTIONS: $U^{+4} + nX^- = UX_n^{+4-n}$

Complex formed	Δ*F*, kcal./mole	Δ*H*, kcal./mole	Δ*S*, cal./deg.mole
USO_4^{+2}	−3.4	−3.2	0.7
$U(SO_4)_2$	−5.3	−2.3	10
$U(SCN)^{+3}$	−2.6	−5.7	−10
$U(SCN)_2^{+2}$	−3.8	−3.9	−0.3

The constants were calculated by the method of Leden.[6] 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. The mathematical treatment of the data in chloride media indicated the formation of two complexes at 25 and 40° but only one at 10°. Ahrland and Larsson[3] reported a value of 2.0 ± 0.5 for the formation of the first

---

(4) R. A. Day, Jr., and R. M. Powers, THIS JOURNAL, **76**, 3895 (1954).

(5) K. A. Kraus and F. Nelson, *ibid.*, **72**, 3901 (1952).

(6) I. Leden, *Z. physik. Chem.*, **A188**, 160 (1941). See also reference 2.

chloride complex at 20° and ionic strength 1.00. They found some slight indication of a second complex under their conditions, but their highest chloride concentration was 0.5 *M*. They suggested that this effect might be attributed to a change in activity coefficients as well as to the formation of a second complex. In our experiments the medium was changed from 2.0 *M* in perchlorate to 2.0 *M* in chloride ion. The effect here may have been brought about by differences in the rate of change of activity coefficients with increase in chloride concentration at different temperatures. If such is the case, better estimates of the values for the formation of UCl^{+3} would be obtained from the data at lower chloride concentrations. These have been estimated as: 1.5 at 40°, 1.8 at 25° and 3.3 at 10°. These values show a consistent change with change in temperature, but are only approximate.

Betts and Leigh[1] reported values of 338 and 250 for the stability constants of the first and second uranium(IV) sulfate complexes at 25° (for the reactions as written in Table II). Sullivan and Hindman,[2] in their recalculation of the data of Betts and Leigh, obtained values for these constants of about 260 and 5400.[7] The values obtained here are somewhat higher than these recalculated values. The first constant is more in line with the original values reported by Betts and Leigh but the results do bear out the contention of Sullivan and Hindman that the second constant is much higher than the value reported by Betts and Leigh. The results here were corrected, by successive approximations, for the amount of complexing agent used up in the reaction.

The results found here for thiocyanate complexes at 25° compare favorably with those of Ahrland and Larsson[3] at 20° and ionic strength 1.00. These workers reported values of 31 and 90 for the first two complexes and an approximate value of 150 for the third complex. They pointed out, however, that they could not definitely prove the existence of the third complex.

Several attempts were made to measure the stability of complexes of uranium(IV) and fluoride ions. Under our usual experimental conditions extremely high distribution ratios were obtained even with low fluoride concentrations. By increasing the TTA concentration to 0.500 *M* a reasonable amount of extraction did occur, but it was not then possible to back-extract uranium(IV) from the aqueous phase. By taking the aqueous phase concentration by difference between the original and final count of the benzene phase, a rough estimate was made of the magnitude of the fluoride constants at 25°. For the reactions written

$$U^{+4} + HF = UF^{+3} + H^+$$
$$U^{+4} + 2HF = UF_2^{+2} + 2H^+$$

(no third complex was considered), the first constant was of the order of 10^6 and the second of 10^8. No account was taken of the decrease in fluoride concentration by complex formation, so these values should undoubtedly be even higher.

Acknowledgment.—This work was supported by the Atomic Energy Commission under Contract No. AT-(40-1)-1350. Some of the preliminary work was done by Mr. Robert M. Powers.

EMORY UNIVERSITY, GEORGIA

---

(7) For the reaction written

$$USO_4^{++} + HSO_4^- = U(SO_4)_2 + H^+$$

the value reported by Betts and Leigh is 0.74 and by Sullivan and Hindman about 21. Our value is about 22.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Observations on the Rare Earths. LXVI.[1] Some Characteristics of Ethylenediaminetetraacetic Acid Chelates of Certain Rare Earth Metal Ions[2]

BY THERALD MOELLER, FRANK A. J. MOSS AND ROBERT H. MARSHALL

RECEIVED DECEMBER 22, 1954

Reaction of oxides of tripositive rare earth metal ions with ethylenediaminetetraacetic acid has been used to prepare moderately strong acids of the type $H[Ln(enta)]\cdot xH_2O$ and salts of the type $Ln[Ln(enta)]_3\cdot yH_2O$. Inclusion of sodium hydroxide in the reaction yields salts of the type $Na[Ln(enta)]\cdot zH_2O$, and reactions of the acids with alkaloids give corresponding alkaloid salts. These compounds have been characterized and related to each other by the physicochemical techniques of *p*H titration, ion migration, X-ray diffraction and differential thermal analysis. Infrared spectra have been interpreted as showing that in species containing the group $[Ln(enta)]^-$ ethylenediaminetetraacetate occupies only five coördination positions and possesses an uncomplexed carboxyl group. Lack of resolution of the potentially asymmetric species $[Y(enta)(H_2O)]^-$ suggests that the bonding is not highly covalent in this ion. Fractional separations of the rare earth elements based upon precipitation of the acids $H[Ln(enta)]\cdot xH_2O$ or crystallization of the sodium salts of these acids are suggested.

Introduction

Since the isolation of the ethylenediaminetetraacetic acid (abbreviated hereinafter H_4enta) derivatives LaH(enta), NdH(enta), and $Y_4(enta)_3\cdot 24H_2O$ by Brintzinger and co-workers,[3,4] the bulk of the published information upon rare earth metal–enta compounds has dealt with the properties of their solutions. Thus, it has been shown that neodymium and enta ions react in solution in a 1:1 stoichiometry,[5] that the presence of enta profoundly affects the absorption spectra of certain rare earth metal ions,[5-7] and that improved separations of the

---

[1] For the preceding paper in this series, see T. Moeller and M. Tecotzky, THIS JOURNAL, **77**, 2649 (1955).

[2] Based upon the doctoral dissertations of F. A. J. Moss, 1952 and R. H. Marshall, 1954, University of Illinois.

[3] H. Brintzinger, H. Thiele and U. Muller, *Z. anorg. allgem. Chem.*, **251**, 285 (1943).

[4] H. Brintzinger and S. Munkelt, *Z. anorg. Chem.*, **256**, 65 (1948).

[5] T. Moeller and J. C. Brantley, THIS JOURNAL, **72**, 5447 (1950).

[6] R. C. Vickery, *J. Chem. Soc.*, 421 (1952).

[7] L. Holleck and D. Eckhardt, *Z. Naturforsch.*, **8a**, 660 (1953); **9a**, 347 (1954); **9b**, 274 (1954).