AEC D-3015

AEC D-3015

THE TRINITRATOURANYL COMPLEX IN KETONIC SOLVENTS

L. Kaplan, R. A. Hildebrandt and M. Ader

October 1, 1950

36114

1

Abstract

The formation of a stable trinitratouranyl anion, $\text{UO}_2(\text{NO}_3)_3^-$, in acetone and methyl isobutyl ketone solutions has been demonstrated spectrophotometrically as well as by studies of solubility, electrolytic transference, and partition between solvents.

This complex is responsible for the enhancement of uranyl nitrate extraction into methyl isobutyl ketone by hydrazine, high molecular weight amines, and quaternary ammonium salts. The stability of the anionic complex has been found to depend on the nature of the associated cation and to decrease with increasing water-content of the solvent. The existence of a stable anionic thorium nitrate complex has been inferred from the effect of thorium nitrate on the spectra of uranyl nitrate solutions, and from the increased extraction of thorium nitrate into methyl isobutyl ketone in the presence of solvent-soluble nitrate salts.

Introduction

The ready solubility of uranyl nitrate in certain organic solvents has long been recognized.¹ A tabulation of its solubility in a number of such solvents has recently been published.² In the course of work at this laboratory on the purification of uranyl nitrate by extraction into methyl isobutyl ketone, it was observed that the extractability was greatly increased when hydrazine was present in the system. It was demonstrated³ that the hydrazine reacted with the ketone to form methyl isobutyl ketazine

CLASSIFICATION CANCELLED

DATE 12-6-50
 FOR THE ATOMIC ENERGY COMMISSION

W. A. Strauser
 CHIEF, DECLASSIFICATION BRANCH

CAUTION

This Document Contains Information Affecting the National Defense of the United States. Its Transmission or the Disclosure of Its Contents in Any Manner to an Unauthorized Person is Prohibited and May Result in Severe Criminal Penalties under Applicable Federal Laws.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

and that the nitrate salt of this base was responsible for the enhanced extraction. The nitrate salts of a number of amines and quaternary ammonium salts were found to exhibit a similar effect on uranium extraction. This report deals with the spectrophotometric and other evidence which has been accumulated regarding the type of complex involved in this phenomenon, and some of the factors affecting complex formation.

Experimental

Solvents: Merck reagent grade acetone was treated with potassium permanganate, distilled, dried over anhydrous potassium carbonate, and redistilled through an efficient column.

Methyl isobutyl ketone (Hexone) from the Shell Chemical Company was converted to the sodium bisulfite addition product from which the ketone was then recovered by steam distillation from potassium carbonate solution, dried over potassium carbonate, and distilled. It was subsequently found that careful fractionation of Shell Hexone under nitrogen gave an equally satisfactory product, and such material was used in several of the experiments.

Cyclohexanone was the Eastman White Label product.

Reagents - Uranyl nitrate hexahydrate was the ether-purified Mallinckrodt product. The dihydrate was obtained by drying the hexahydrate in vacuo over sulfuric acid. The water contents of these hydrates were checked by Karl Fischer titration.

Tetra-n-butyl and tetra-n-propylammonium nitrates were prepared by the procedure of Tucker and Kraus.⁴ The former melted at 118.5-119.5°; the latter decomposed at 260-261°.

Methyl isobutyl ketazine was prepared in 89% yield by refluxing 85% hydrazine hydrate with a two-fold excess of methyl isobutyl ketone. The product boiled at 117-119°/27 mm; 218°/740 mm.⁵ Anal. Calc. for C₁₂H₂₄N₂:N, 14.27%; Found: N, 14.19%.

Pyridinium nitrate was prepared by adding one equivalent of concentrated nitric acid to a solution of pyridine in ether. The precipitated salt was washed with ether and dried in vacuo.

2-n-hexylpyridine from the Reilly Chemical Company was fractionated, and the fraction distilling at 218-221°/745 mm. was used. Other amines used were redistilled Eastman products.

Analytical procedures. Uranium was determined, for the distribution and electrolytic transference experiments, by a colorimetric procedure using potassium ferrocyanide. Where uranium-233 was used as a tracer, its concentration was measured by alpha-counting in a 52% geometry proportional counter.

Spectrophotometric measurement. Absorption spectra were measured with a Beckman model DU quartz spectrophotometer using matched 1 cm. Corex cells. Solutions were compared against the pure solvent. Where necessary, the readings were corrected for the slight absorption by reagents other than uranyl nitrate present in the solution. Solutions were prepared by accurately weighing the crystalline uranyl nitrate and quaternary ammonium salts and making up to volume with the solvent or solvent mixture. Solutions containing tertiary ammonium nitrates were prepared from equivalent quantities of the amine and 16 M aqueous nitric acid. Concentrations reported are volume molar. Except where otherwise noted, the solutions were 0.02 M in uranyl nitrate hexahydrate.

Calculations

For an association reaction

where A and C absorb light unequally and B does not absorb, the relative amounts of A and C in solution and the association constant for the reaction may be readily calculated from the measured optical densities. Let

~~SECRET~~

(A), (C) = molar concentrations of A and C, respectively

$$A_0 = (A) + (C)$$

$$\alpha = (C)/A_0$$

D = measured optical density of a solution in a 1 cm. cell

D₀ = density in the absence of B

D_c = density in the presence of a large excess of B

E, E₀, E_c = corresponding molar extinction coefficients

$$\text{Then } D = E_0 (A) + E_c (C) \quad (1)$$

$$D = E_0 (A_0 - C) + E_c (C) \quad (2)$$

$$D = E_0 A_0 + (E_c - E_0) (C) \quad (3)$$

$$(C) = \frac{D - E_0 A_0}{E_c - E_0} = \frac{D - D_0}{E_c - E_0} \quad (4)$$

$$\alpha = (C)/A_0 = \frac{D - D_0}{D_c - D_0} \quad (5)$$

The association constant, K, if the activity coefficients are taken equal to unity, is given by

$$K = \frac{(C)}{(A) (B)^n} \quad (6)$$

$$K = \frac{\alpha}{1 - \alpha} \cdot \frac{1}{(B)^n} \quad (7)$$

Results and Discussion.

Spectrophotometric evidence for a trinitrate complex. The absorption spectra of solutions of uranyl nitrate in acetone, in methyl isobutyl ketone, and in cyclohexanone (Fig. 1) are very much alike. In each case a broad absorption band extends from about 490 mμ to about 380 mμ, with a maximum close to 426 mμ. At shorter wave lengths the absorption again increases, the rate of increase becoming very great below 340 mμ. Superimposed on this continuum are quite distinct

maxima at about 360, 370, 426, 440, 455 and 470 m μ ; less well-defined discontinuities occur between 370 and 426 m μ . The solutions in methyl isobutyl ketone follow Beer's law fairly closely: the molar extinction coefficient of a 0.1 M solution deviates from that of a 0.02 M solution by + 8% at 470 m μ and - 6% at 360 m μ , intermediate wave lengths falling between these two values. No Beer's law studies were made in acetone or cyclohexanone.

The addition of tetrabutylammonium nitrate to a solution of uranyl nitrate in acetone produces a marked change in the spectrum (Fig. 1), particularly in the portion above 420 m μ . The four peaks in this region are greatly intensified, without undergoing any pronounced shift in wave length. The extinction at each peak increases linearly with the tetrabutylammonium nitrate concentration until the latter equals that of the uranyl nitrate; further addition of tetrabutylammonium nitrate produces very little additional effect. A similar effect at these wave lengths is obtained in methyl isobutyl ketone and in cyclohexanone, the enhanced spectrum being almost identical in each solvent (Table 1). The spectrum in the presence of tetrabutylammonium nitrate can be duplicated by substituting for it such nitrates as tributylammonium, pyridinium or methyl isobutyl ketazinium.

The fact that a number of nitrate salts cause the same changes in the spectrum of uranyl nitrate solutions, and that almost the maximum effect is produced by an equimolar quantity of the nitrate is good evidence for the formation of a stable 1:1 complex between uranyl nitrate and nitrate ion, i.e.,

The formula of the complex was further verified by application of the method of continuous variations⁶ to solutions of uranyl nitrate and tetrabutylammonium nitrate in methyl isobutyl ketone. Solutions, 0.05 M in each of these salts, were mixed, in varying proportions, to a total volume of 10 ml. The optical

Table 1
The Effect of Nitrate Salts, RNO_3 , on the Absorption
of Uranyl Nitrate in Ketone Solutions

Solvent	R	(RNO_3) mols/liter	λ_{max} m μ	E max	λ_{max} m μ	E max	λ_{max} m μ	E max
Acetone	$\text{Bu}_4\text{N}^{(c)}$	0.01	471	4.1	455	7.0	440	10.0
			470	12.0	455	18.9	441	18.2
	Bu_4N	0.02	470	19.8	455	30.5	441	26.6
	Bu_4N	0.04	470	19.8	455	30.6	441	27.5
M.I.B.K. (a)			470	3.6	454	6.0	440	10.2
	Bu_4N	0.01	471	12.7	456	19.9	441	20.2
	Bu_4N	0.02	471	20.8	456	31.8	441	29.2
	Bu_4N	0.04	471	19.8	456	31.0	442	26.5
	$\text{Bu}_3\text{NH}^{(d)}$	0.04	472	19.8	456	31.0	442	26.5
	$\text{C}_5\text{H}_5\text{NH}^{(e)}$	0.04	471	20.4	456	30.8	441	27.3
	$\text{C}_{12}\text{H}_{24}\text{N}_2\text{H}^{(f)}$	0.04	471	19.8	456	30.0	441	27.0
	Li	(h)	471	9.2	456	14.7		
	Na	(h)	471	8.8	456	12.2		
C.H. (b)			471	4.2	455	6.4	441	9.6
	$\text{Et}_3\text{NH}^{(g)}$	0.02	471	16.8	456	27.0	441	22.5
		0.04	471	18.3	456	29.7	441	25.0

[U] = 0.02 M

- (a) methyl isobutyl ketone
- (b) cyclohexanone
- (c) tetra-n-butylammonium
- (d) tri-n-butylammonium
- (e) pyridinium
- (f) methyl isobutyl ketazinium
- (g) triethylammonium
- (h) saturated solution

density of each mixture was determined at 455 and 470 mμ. From each observed density was subtracted the density calculated for that mixture assuming no interaction between the reagents. The results are recorded in Table 2. In Figure 2, the increase in density is plotted against the ratio of uranyl nitrate concentration to the sum of the concentrations of the two salts. The points for each wave length fall very close to straight lines which intersect at a ratio of 0.50, i.e., an equimolar mixture of the two salts. The absence of curvature in the plots bespeaks a very high degree of stability for the complex: the difference between the observed density of the equimolar mixture, at each wave length and that corresponding to the intersection of the two lines corresponds to an association constant of about 8×10^4 for the complex.

The formula deduced for the complex is independent of any assumptions regarding the dissociation of uranyl nitrate in the absence of added nitrate, since the maximum extinction occurs when there is a total of three nitrate ions for each uranyl ion in solution.

Complex formation with nitric acid. The addition of increments of concentrated aqueous nitric acid to a 0.02 M solution of uranyl nitrate in methyl isobutyl ketone causes a gradual increase in absorption at the four peaks between 420 and 480 mμ. In contrast to the results with tetrabutylammonium nitrate and similar salts the effect is not stoichiometric. At a nitric acid concentration of 0.78 M the increase in absorption is only about half of that produced by 0.02 M tetrabutylammonium nitrate. The optical densities of a series of solutions, measured at two wave lengths, are recorded in Table 3. The fraction of the uranium complexed, α , is calculated using equation (5). The association constant, K, is calculated by equation (7) for the assumed reaction

The value of D_c is that obtained with an excess of tetrabutylammonium nitrate.

Table 2

Absorption by Various Mixtures of Uranyl Nitrate
and Tetrabutylammonium Nitrate in Methyl Isobutyl Ketone

χ	$\lambda = 455 \text{ m}\mu$		$\lambda = 470 \text{ m}\mu$	
	D	Y	D	Y
0	0.022	0.000	0.020	0.000
0.1	0.183	0.131	0.120	0.084
0.2	0.337	0.257	0.214	0.161
0.3	0.516	0.406	0.326	0.257
0.4	0.643	0.504	0.420	0.335
0.5	0.800	0.631	0.509	0.407
0.6	0.720	0.523	0.460	0.343
0.7	0.618	0.392	0.385	0.251
0.8	0.511	0.255	0.306	0.156
0.9	0.410	0.125	0.247	0.080
1.0	0.315	0.000	0.183	0.000

$$\chi = \frac{\text{Vol. of uranyl nitrate solution}}{\text{total volume}}$$

$$Y = D_{\chi} - \chi D_1 - (1 - \chi) D_0$$

SECRET

Table 3

Reaction Between Uranyl Nitrate and Nitric Acid
in Methyl Isobutyl Ketone

(HNO ₃) mols/liter	(Bu ₄ NHNO ₃) mols/liter	$\lambda = 454 \text{ m}\mu$		$\lambda = 469 \text{ m}\mu$		$\alpha(\text{mean})$	K
		D	α	D	α		
0		0.124	0.000	0.075	0.000		
0.0078		0.127	0.006	0.075	0.000		
0.046		0.142	0.037	0.086	0.034	0.035	0.8
0.116		0.180	0.116	0.110	0.108	0.112	1.1
0.31		0.250	0.26	0.160	0.26	0.26	1.1
0.78		0.380	0.53	0.252	0.55	0.54	1.5
1.56		0.432	0.64	0.275	0.62	0.63	1.0
0	0.04	0.610	1.00	0.400	1.00	1.00	
0.78	0.03	0.481	0.74	0.310	0.72	0.73	
0.78	0.10	0.579	0.94	0.375	0.92	0.93	
0.78	0.25	0.595	0.97	0.393	0.98	0.98	
1.56	0.06	0.479	0.73	0.310	0.72	0.73	
1.56	0.19	0.523	0.82	0.345	0.83	0.83	
Mean 1.1 ± 0.2							

$$[U] = 0.0200 \text{ M}$$

α = fraction of uranium complexed

$$K = \frac{\alpha}{1 - \alpha} \cdot \frac{1}{(\text{HNO}_3)}$$

The close agreement between the results at the two maxima, using the extinction coefficients for the complex with tetrabutylammonium nitrate, is evidence that the complex formed with the acid is similar to that formed with the salt. The relatively small variation in the association "constant" over the wide range of nitric acid concentration is rather surprising, considering the large amount of water introduced into the solution with the acid. (The molar concentration of water is about 1.6 times that of the acid). The low value of the constant, compared with that for the tetrabutylammonium nitrate complex, may be due in part to the presence of water in the system, although this effect should be quite small at the lower acid concentrations. That it is not entirely due to this factor is shown by the large further increase in absorption produced by the addition of tetrabutylammonium nitrate in concentrations small compared to that of the nitric acid already in the system. It is also evident that the tetrabutylammonium nitrate, although much more effective than nitric acid in causing complex formation, is considerably less effective in solutions containing high acid and water concentration than it is in their absence. However, the close agreement of the spectrum at the highest tetrabutylammonium nitrate concentration with that of the complex in nitric acid-free methyl isobutyl ketone is evidence that there is little if any effect of the medium on the spectrum of the complex in these systems.

Differences in the effectiveness of complexing agents. In acetone solution, as previously mentioned, 0.02 M tetrabutylammonium nitrate complexes almost quantitatively an equimolar amount of uranyl nitrate. Tetra-n-propyl ammonium nitrate behaves identically. With the nitric acid salt of the tertiary amine, 2-n-hexylpyridine, however, complexing is not so complete. In a 0.02 M uranyl nitrate solution, 0.01 M or 0.04 M concentrations of this reagent give absorption at the characteristic maxima corresponding, within experimental error, to complete reaction; 0.02 M 2-hexylpyridinium nitrate gives only 88% complexing.

The lesser effectiveness of this tertiary ammonium salt, compared to the quaternary salts, cannot be attributed to the acid-base dissociation,

since the addition of nitric acid, which would reverse this reaction, has no effect on the absorption. The association constant calculated for the complex with 2-hexylpyridinium nitrate is about 3×10^3 ; the constants for the tetrapropyl- and tetrabutylammonium salts appear to be at least 10^5 . The data are summarized in Table 4. The fraction complexed is calculated by equation (5); the difference between the absorption at each peak and that at an adjacent minimum is used in order to minimize the possibility of errors caused by turbidity in the solution, differences in absorption in the cell walls, or variations in the absorption by the reagents.

In methyl isobutyl ketone, similarly, it has been observed that pyridinium nitrate is a less effective complexing agent than is tetrabutylammonium nitrate, and this difference is not affected by the addition of excess nitric acid.

Discussion of the Cation Effect. The differences in the effectiveness of various nitrates with respect to the formation of the trinitrato uranyl complex is probably related to their relative ionization in the solvent. Consider the equilibria (neglecting solvation)

Table 4

Complex Formation of Uranyl Nitrate with Some Substituted
Ammonium Nitrates, RNO_3 , in Acetone

R	(RNO_3) moles/l.	(HNO_3) moles/l.	$D_{441}-D_{434}$	α	$D_{455}-D_{448}$	α	$\alpha(\text{mean})$
$Pr_4N^{(a)}$			0.012		0.042		
	0.010		0.182	0.51	0.278	0.52	0.52
	0.020		0.342	0.99	0.497	1.00	1.00
	0.040		0.345	1.00	0.495	1.00	1.00
$Bu_4N^{(b)}$	0.010		0.179	0.51	0.280	0.52	0.52
	0.020		0.340	1.00	0.506	1.01	1.01
	0.040		0.341	1.00	0.501	1.00	1.00
$C_{11}H_{17}NH^{(c)}$	0.010		0.177	0.49	0.275	0.51	0.50
	0.020		0.307	0.87	0.451	0.89	0.88
	0.040		0.348	1.00	0.503	1.00	1.00
	0.020	0.010	0.305	0.87	0.451	0.89	0.88
	0.020	0.020	0.306	0.87	0.451	0.89	0.88
$[U] = 0.02 \text{ M}$							

(a) tetra-n-propylammonium

(b) tetra-n-butylammonium

(c) 2-n-hexylpyridinium

For a given nitrate, RNO_3 , the association constant $K_6 = K_5 \frac{K_7}{K_8} \cdot K_5$ is independent of the nature of R; K_7/K_8 is the ratio of the ionization constant of RNO_3 to that of its complex salt with uranyl nitrate. The ionization constant of an electrolyte RX in a solvent of low dielectric constant is, according to Bjerrum,⁷ a function of the dielectric constant and of the effective diameter "a" of the ion pair. The "a" value increases with the radius of the ions and with their symmetry. It is to be expected that the large ion $UO_2(NO_3)_3^-$ would form ion pairs with larger "a" values than the corresponding ion pairs containing NO_3^- . Thus, the ratio K_7/K_8 is less than unity; i.e., in a given solvent the nitrate ion is a more effective complexing agent than is a nitrate salt or nitric acid. The difference in behavior among the various nitrates must be attributed to a change in the ratio K_7/K_8 as the nature of R changes. It is known that substituted ammonium salts containing one or more hydrogen atoms attached to the nitrogen have much lower ionization constants than have the quaternary salts. For example,⁸ in nitrobenzene, trimethylammonium picrate has a constant of 1.5×10^{-4} while that of tetramethylammonium picrate is 4×10^{-2} ; in ethylene chloride the constants for pyridinium nitrate⁹ and tetra-n-butylammonium nitrate¹⁰ are 6×10^{-7} and 1.18×10^{-4} , respectively. The lower ionization of the tertiary ammonium salts has been ascribed⁸ at least in part to hydrogen bonding with the negative ion. In the $UO_2(NO_3)_3^-$ ion, the negative charge is distributed over a larger number of oxygen atoms than in the nitrate ion, and one would therefore expect the hydrogen bonding to be greatly diminished. The 2-hexylpyridinium trinitratouranyl compound should, then, be more highly ionized than the nitrate, because of both diminished coulombic attraction and diminished hydrogen bonding. The increase in ionization should be greater than that for the tetrabutylammonium compounds, where only coulombic forces are involved. The smaller value of K_7/K_8 for the 2-hexylpyridinium compounds than for the tetrabutylammonium compounds would result in a lower K_6 for the former, i.e., lower complexing effectiveness, as was actually observed.

A similar argument can be applied to nitric acid and to its complex with uranyl nitrate, leading to the conclusion that the trinitratouranic acid should be a much stronger acid than nitric acid in solvents of low dielectric constant, and that, therefore, nitric acid should show relatively little tendency to form the trinitrato complex.

The discussion above has assumed implicitly that the bulk of the electrolytes in the solution were in the unionized form. Actually, tetrabutylammonium nitrate in acetone has a dissociation constant¹¹ of 5.46×10^{-3} , so that a 0.02 M solution would be about 40% ionized; the trinitratouranyl salt would probably be even more highly ionized. Since the spectrophotometric measurements do not distinguish between the ions and unionized electrolytes in the solution, the apparent association constants reported are a composite of those for the ions and those for the unionized electrolytes in the particular solution studied. Although this complicates the quantitative study of the relative effectiveness of different nitrates as complexing agents for uranyl nitrate, it does not affect the qualitative conclusions reached in the preceding paragraphs. That the spectra of the ionized and unionized complex are not markedly different, at least in the region of the strong absorption bands, is shown by the close similarity of the spectra obtained with a number of different cations, and in solvents of varying dielectric constant.

The ionization of uranyl nitrate in ketonic solvents. In acetone, with a dielectric constant¹¹ of 20.5 at 25°, strong electrolytes may be fairly highly ionized. Tetra-n-butylammonium nitrate, as previously mentioned, has an ionic dissociation constant of 5.46×10^{-3} ; the picrate has a constant of 2.23×10^{-2} . These correspond, in 0.02 M solution, to about 40% and 65% ionization, respectively. It is of interest to consider the possible ionization of uranyl nitrate according to the equation $\text{UO}_2(\text{NO}_3)_2 \rightleftharpoons \text{UO}_2\text{NO}_3^+ + \text{NO}_3^-$. (IX)

A maximum value for the equilibrium constant for this reaction may be estimated

from a consideration of complex ion formation

$$K_9 = \frac{(\text{UO}_2\text{NO}_3^+) (\text{NO}_3^-)}{[\text{UO}_2 (\text{NO}_3)_2]}$$

$$K_2 = \frac{[\text{UO}_2(\text{NO}_3)_3^-]}{[\text{UO}_2(\text{NO}_3)_2] (\text{NO}_3^-)}$$

Then for the disproportionation

$$K_{10} = K_9 K_2 = \frac{(\text{UO}_2\text{NO}_3^+) [\text{UO}_2(\text{NO}_3)_3^-]}{[\text{UO}_2(\text{NO}_3)_2]^2} \quad (8)$$

The value of K_2 may be estimated to be of the order of 10^5 , from the results of spectrophotometric measurements on uranyl nitrate-tetrabutylammonium nitrate solutions. The concentration of UO_2NO_3^+ may be set equal to that of $\text{UO}_2(\text{NO}_3)_3^-$. Although one cannot, from the absorption spectra, obtain reliable values for the concentrations of the various uranium species in the solution, it appears to be possible to fix a maximum value for the concentration of the $\text{UO}_2(\text{NO}_3)_3^-$ ion.

Let us assume that the absorption of UO_2NO_3^+ is not very much different from that of $\text{UO}_2(\text{NO}_3)_2$ at the peaks characteristic of the $\text{UO}_2(\text{NO}_3)_3^-$ ion and that in the uranyl nitrate solution all of the difference in absorption between each maximum and the adjacent minimum of shorter wave length is due to $\text{UO}_2(\text{NO}_3)_3^-$. One may then calculate the concentration of the latter, using equation (4). The results obtained for the peaks at 470, 455, and 441 mμ in a 0.02 M solution are 0.002, 0.0017 and 0.0014 M $\text{UO}_2(\text{NO}_3)_3^-$, respectively. (It should be emphasized that these relatively low peaks are more probably characteristic of $\text{UO}_2(\text{NO}_3)_2$,¹² and the $\text{UO}_2(\text{NO}_3)_3^-$ concentration may be much lower than indicated.) Using the highest value, 0.002, leads to a maximum value of $K_9 K_2$ of 1.5×10^{-2} . Taking K_2 as 10^5 ,

K_9 equals 1.5×10^{-7} . Uranyl nitrate is thus a very weak electrolyte in acetone, with respect to ionization according to equation (9). Disproportionation according to (10) is a much more probable mechanism for the formation of ionic species which may exist in solution. (Considering the ionization

instead of (IX) would not affect the conclusion reached above but only the constants assigned to the various steps.)

Because of the very close similarity of the spectra of uranyl nitrate and of the trinitrato complex in methyl isobutyl ketone and cyclohexanone to those in acetone the same general conclusions may be applied to solutions in these solvents.

Other evidence for the trinitratouranyl ion: Solubility measurements.

The formation of a complex AB between two substances A and B in solution should cause an increase in the apparent solubility of A in the presence of B, provided that AB is more soluble than A in the solvent. Because of the high solubility of uranyl nitrate in methyl isobutyl ketone, it was convenient to study the effect of uranyl nitrate concentration on the solubility of more difficultly soluble nitrates. The solubility of the moderately soluble pyridinium nitrate in methyl isobutyl ketone at $25 \pm 1^\circ$ was estimated at several concentrations of uranyl nitrate dihydrate by gradually adding crystals until no more would dissolve and weighing the excess. The data in Table 5 show a marked increase in solubility in the presence of uranyl nitrate. The observation that the increase in solubility is somewhat greater than the uranyl nitrate concentration is not explained. It may be the result of the crudeness of the measurements.

Somewhat more accurate measurements were made of the solubility of ammonium nitrate in methyl isobutyl ketone at various concentrations of uranyl

Table 5

Solubility of Pyridinium Nitrate in Methyl Isobutyl Ketone
Containing Uranyl Nitrate at $25 \pm 1^\circ$

$[\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}]$ moles/l.	$(\text{C}_5\text{H}_5\text{NHNO}_3)$ Moles/l.	Increase
0	0.0163	
0.0200	0.0382	0.0219
0.0500	0.0693	0.0530
0.100	0.133	0.117

nitrate hexahydrate. A solution of the uranyl nitrate was saturated with ammonium nitrate at $26 \pm 1^\circ$. The uranium was determined colorimetrically and the ammonia by Kjeldahl distillation. The results in Table 6 show an increase in solubility approaching the concentration of uranyl nitrate at low concentrations, the ratio of ammonium nitrate to uranyl nitrate falling off at higher concentrations. Although in principle it should be possible to estimate an equilibrium constant for the reaction

from these data, the uncertainty in the solubility of ammonium nitrate in pure methyl isobutyl ketone and the lack of knowledge regarding the ionization of the various species make this impractical.

Electrical transference. The complexing of uranium as an anion should result in its migration toward the anode under the influence of an electric field. This effect has been confirmed for solutions of uranyl nitrate in methyl isobutyl ketone in the presence of triethylammonium nitrate or tetrabutylammonium nitrate.

Table 6

Solubility of Ammonium Nitrate in Methyl Isobutyl Ketone in the Presence of Uranyl Nitrate

$[UO_2(NO_3)_2 \cdot 6H_2O]$ Moles/l.	(NH_4NO_3) Moles/l.
0	ca. 2×10^{-4}
0.0114	0.0105
0.0212	0.0180
0.0480	0.0295
0.114	0.0605

The transference cell used was that described by McLane, Dixon and Hindman,¹³ except that platinum electrodes were used and the electrode compartments were filled with the methyl isobutyl ketone solution being studied. In one experiment a 0.1 M solution of triethylammonium nitrate in methyl isobutyl ketone was placed in the electrode compartments and a similar solution containing in addition 0.01 M uranyl nitrate hexahydrate was placed in the center compartment. After electrolysis for two hours at a current of 0.2 milliamperes, 76% of the uranium had migrated from the center compartment. Of this, 2.6% was found in the cathode compartment and 97.4% in the anode compartment. Since some electrosmosis was observed under these conditions, an experiment was performed using 0.05 M tetrabutylammonium nitrate; the center compartment contained, in addition, uranyl nitrate prepared from 20 μ g of uranium -233. Electrolysis for 2.5 hours at 0.6 milliamperes resulted in the migration of 83% of the uranium (determined by alpha-counting) out of the center compartment. Of the uranium transferred, 99.9% was found in the anode portion and only 0.1% in the cathode portion. Electrosmosis was negligible.

For comparison, an electrolysis was carried out in 1 M aqueous nitric acid. After 20 hours at 10 milliamperes, 43% of the uranium had left the center compartment; 99.8% of this was found in the cathode portion and 0.2% in the anode portion.

Distribution between immiscible liquids. The distribution of a substance between two liquid phases will be affected if it undergoes reaction with a constituent of either phase. From the dependence of the distribution ratio on the concentration of the reactants it is possible to calculate the mol ratio of the reactants in the compound formed and the equilibrium constant for the reaction.

If uranyl nitrate reacts with another nitrate, RNO_3 , in an organic solvent according to equation (VI) the extraction of uranyl nitrate into the solvent from an aqueous solution will be enhanced by the addition of RNO_3 , provided that $RUO_2(NO_3)_3$ distributes into the organic solvent more effectively than does $UO_2(NO_3)_2$.

Let

(UN_2) = concentration of uranyl nitrate

(RUN_3) = concentration of the complex

(RN) = concentration of RNO_3

(U) = total uranium concentration

$$Q = \frac{(U)_{org}}{(U)_{aq}}$$

Q_0 = Q in the absence of RNO_3

$$Q_{RN} = \frac{(RN)_{org}}{(RN)_{aq}}$$

where the subscripts org and aq refer to the organic and aqueous phases, respectively. If the addition of RN causes no change in the uranium species in the aqueous phase, we may write

$$K = \frac{(RN_3)_{org}}{(UN_2)_{org} (RN)_{org}} \quad (9)$$

$$Q_o = \frac{(UN_2)_{org}}{(U)_{aq}} \quad (10)$$

$$\text{Since } (U)_{org} = (UN_2)_{org} + (RN_3)_{org} \quad (11)$$

$$Q = \frac{(UN_2)_{org} + (RN_3)_{org}}{(U)_{aq}} \quad (12)$$

$$Q = \frac{(UN_2)_{org} + K (UN_2)_{org} (RN)_{org}}{(U)_{aq}} \quad (13)$$

$$Q = Q_o [1 + K (RN)_{org}] \quad (14)$$

$$\frac{Q - Q_o}{Q_o} = K (RN)_{org} \quad (15)$$

The concentration of RNO_3 in the organic phase is determined by its distribution ratio

$$Q_{RN} = \frac{(RN)_{org}}{(RN)_{aq}}$$

For unit volume of each phase, the total added RNO_3 is given by

$$(RN)_{tot} = (RN)_{aq} + (RN)_{org} + (RN_3)_{org} \quad (16)$$

so that

$$(RN)_{org} = \frac{Q_{RN}}{1 + Q_{RN}} [(RN)_{tot} - (RN_3)_{org}] \quad (17)$$

$$\text{Then } \frac{Q - Q_o}{Q_o} \cdot \frac{1}{(RN)_{tot} - (RN_3)_{org}} = \frac{Q_{RN}}{1 + Q_{RN}} K = K^1 \quad (18)$$

The system chosen for this study consisted of equal volumes of an aqueous solution 8 M in ammonium nitrate, 0.4 M in nitric acid, and 0.02 M in uranyl nitrate, and of a methyl isobutyl ketone solution of a substituted ammonium nitrate. Ammonium nitrate is not appreciably extracted into methyl isobutyl ketone in such a system; the substituted ammonium nitrate distributes between the two

phases to an extent depending largely on the size of the organic substituents. Since the distribution ratio for uranium in this system is not sensitive to a small increase in ammonium nitrate concentration nor to a considerable decrease in the uranyl nitrate concentration, it is assumed that any equilibria in the aqueous phase involving uranium are not affected by the addition of a small amount of the substituted ammonium nitrate nor by extraction of part of the uranium. (This is equivalent to the assumption of constant activity coefficient for the uranium in the aqueous phase.)

The results with a number of substituted ammonium nitrates are recorded in Table 7. The values of K^1 are calculated by equation (18), using values of $(\text{RUN}_3)_{\text{org}}$ calculated with equations (2) and (3). The large effect of a number of the salts on the distribution of uranium, and the relatively constant value of K^1 for a given salt, support the assumption that the salts react with uranyl nitrate by equation (I). The distribution of the individual substituted ammonium nitrates (Q_{RN}) between the two phases was not measured, because of analytical difficulties. However, it was qualitatively observed that the first four salts in the table went preferentially into the organic phase, while the last three favored the aqueous phase. The low values of K^1 for the latter are undoubtedly attributable to their low concentrations in the organic phase. The variations in K^1 among the first four salts are due in part to variations in Q_{RN} ; the high value for tetrabutylammonium nitrate, compared to the others, probably involves also the specific cation effects previously discussed. Since Q_{RN} for tetrabutylammonium nitrate is greater than 1, the association constant, K , for this salt is less than twice K^1 . This value is considerably lower than that estimated spectrophotometrically. The difference involves the effect of water on the equilibrium (see below), since the spectrophotometric measurements were made in dry methyl isobutyl ketone, while the solvent used in the distribution experiments was, of course, water-saturated.

Table 7

Extraction of Uranyl Nitrate by Methyl Isobutyl Ketone
In the Presence of Substituted Ammonium Nitrates (RNO_3)

R	$(\text{RN})_{\text{tot}} \times 10^2$	$(\text{U})_{\text{aq}} \times 10^3$	$(\text{U})_{\text{org}} \times 10^3$	Q	Q-Q ₀	$(\text{UN}_2)_{\text{org}} \times 10^3$	$(\text{RUN}_3)_{\text{org}} \times 10^3$	K'
	0	5.8	15.2	2.62				
$(\text{C}_4\text{H}_9)_3\text{NH}^{(a)}$	2.1	2.90	18.0	6.2	3.6	7.6	10.4	130
	4.2	1.80	19.2	10.7	8.1	4.7	14.5	110
	11.0	0.60	19.4	32.4	29.8	1.6	17.8	120
	21.0	0.29	19.6	68	66	0.7	18.9	130
$(\text{C}_8\text{H}_{17})_2\text{NH}_2^{(b)}$	2.5	3.0	18.0	6.0	3.4	7.8	10.2	88
	5.0	2.0	18.8	9.4	6.8	5.2	13.6	73
	10.0	1.2	19.8	16.5	13.9	3.1	15.7	65
	20.0	0.60	19.8	33	30	1.6	18.2	65
$(\text{C}_{11}\text{H}_{15})\text{NH}^{(c)}$	2.0	3.3	17.8	5.4	2.8	8.6	9.2	100
	5.0	1.4	18.8	13.4	10.8	3.6	15.2	120
	10.0	0.75	20.0	26.7	24	2.0	18.0	110
	20.0	0.34	19.3	57	54	0.9	18.4	110
$\text{C}_{12}\text{H}_{24}\text{N}_2\text{H}^{(d)}$	2.1	2.90	15.9	5.5	2.9	7.6	8.3	86
	10.5	0.73	18.7	25.6	23.0	1.9	16.8	100
$(\text{C}_4\text{H}_9)_4\text{N}^{(e)}$	10.0	0.20	19.4	97	94	0.5	18.9	440
	10.0	0.23	19.3	84	81	0.6	18.7	380
$\text{C}_6\text{H}_7\text{NH}^{(f)}$	10.0			2.8	0.2			0.8
$(\text{C}_2\text{H}_5)_3\text{NH}^{(g)}$	10.0			4.0	1.4			5.4
$(\text{C}_2\text{H}_4\text{OH})_4\text{N}^{(h)}$	10.0			2.67	0.05			0.2
Aqueous phase: 8 M NH_4NO_3 , 0.4 M HNO_3								

- (a) tri-n-butylammonium
 (b) di-2-ethylhexylammonium
 (c) 2-n-hexylpyridinium
 (d) methyl isobutyl ketazinium
 (e) tetra-n-butylammonium
 (f) 2-methylpyridinium
 (g) triethylammonium
 (h) tetrahydroxyethylammonium

Further evidence that the distribution effect is due to the same cause as the spectral changes was obtained by examining the spectra of the extracts obtained in the absence and presence of tetrabutylammonium nitrate. These spectra are quite similar to those in dry methyl isobutyl ketone in the absence, and in the presence of an excess, of the quaternary salt, respectively. It is also of interest that the addition of tetrabutylammonium nitrate to an aqueous solution of the composition used in the distribution measurements causes almost quantitative precipitation of the uranium. The precipitate dissolves readily in methyl isobutyl ketone to give a solution whose spectrum is identical with that of the trinitratouranyl complex. The enhanced extraction caused by tetrabutylammonium nitrate is thus clearly the result of the formation of a compound, stable and soluble in the organic phase but difficultly soluble in the aqueous phase.

Evidence for an anionic thorium nitrate complex. In contrast to most of the other soluble nitrates studied, the addition of ~~thorium nitrate~~ to a solution of ~~uranyl nitrate~~ in methyl isobutyl ketone does not cause an intensification of the four absorption peaks characteristic of the trinitratouranyl complex. In the presence of a nitrate which does produce such an intensification, on the other hand, the addition of ~~thorium nitrate~~ causes a marked decrease in absorption. In Table 8, data is presented showing the effect of the addition of ~~thorium nitrate~~ on the absorption of a ~~uranyl nitrate-triethylammonium nitrate~~ solution. The agreement between the concentrations of trinitratouranyl complex calculated at two wave lengths by equation (11) is evidence that ~~thorium nitrate~~ competes with ~~uranyl nitrate~~ for the available excess nitrate ion:

the data are insufficient to permit the calculation of the formula of the thorium complex. At the concentrations used in the experiments, the ~~thorium nitrate~~ complex is considerably more stable than the trinitratouranyl complex.

Table 8

Effect of Thorium Nitrate on the Spectrum of Uranyl Nitrate
in Methyl Isobutyl Ketone

UO ₂ (NO ₃) ₂ Moles/l.	Th(NO ₃) ₄ Moles/l.	(C ₂ H ₅) ₃ NHNO ₃ Moles/l.	λ = 471 mμ		λ = 456 mμ	
			D	α	D	α
0.020	0.000	0.000	0.085	0	0.136	0
0.020	0.000	0.021	0.395	1.00	0.61	1.00
0.020	0.025	0.020	0.137	0.17	0.215	0.17
0.020	0.040	0.021	0.120	0.11	0.185	0.10

$$\alpha = \frac{[\text{UO}_2(\text{NO}_3)_3^-]}{(\text{U})_{\text{total}}}$$

Further evidence for a stable anionic thorium nitrate complex was obtained from partition studies. The distribution ratio of thorium nitrate between an aqueous solution, 8 M in ammonium nitrate and 0.2 M in nitric acid, and methyl isobutyl ketone is 0.041. In the presence of 0.1 M methyl isobutyl ketazinium nitrate, this increases to 27. Under the same conditions the distribution of uranyl nitrate increases from 2.66 to 25.6.

The effect of water on complex ion formation. As previously noted, the addition of 0.02 M tetrabutylammonium nitrate to a 0.02 M uranyl nitrate solution in acetone causes practically quantitative conversion to the trinitrate complex, as evidenced by the characteristic absorption maxima. The presence of water in such a solution markedly diminishes the extent of trinitrate formation. As shown in Table 9, a solution containing 10% by weight of water gives an absorption spectrum indicating only about 15% trinitrate formation; with 20% water, there is no evidence for the trinitrate. It is unlikely that the increase in dielectric constant caused by the addition of water is entirely responsible for this effect.

Table 9

Effect of Water on Complex Formation in Acetone

Bu ₄ NNO ₃ Moles/l.	H ₂ O %	D ₄₇₀	α	D ₄₅₅	α
0	0	0.081	0	0.140	0
0.020	0	0.395	1.00	0.610	1.00
0.020	10	0.126	0.14	0.216	0.16
0.020	20	0.075	0	0.140	0

$$U_{\text{total}} = 0.02 \text{ M}$$

The dielectric constants¹¹ for pure acetone, 10% water, and 20% water are, respectively, 19.1, 24.0, and 29.6. In nitroethane, with a dielectric constant of 30, the trinitrate complex is very stable¹². It is much more likely that the effect of water is due to a competition between water and nitrate ion for a position in the inner coordination sphere of the uranyl ion. One cannot determine from the data the number of water molecules displaced by the third nitrate ion, nor does one know the number of ketone molecules coordinated with either the uranyl nitrate molecule or the trinitrato-uranyl ion.

Acknowledgement. The authors are indebted to Mr. H. H. Hyman for his helpful suggestions during the course of this work.

References

- (1) See Gmelins Handbuch der Anorganischen Chemie, System Nummer 55, p.117 (1936)
- (2) Yaffe, Can. Jour. Res., Sec. B, 27, 638 (1950).
- (3) Kaplan, Unpublished work.
- (4) Tucker and Kraus, J. Am. Chem. Soc., 69, 454 (1947).
- (5) Mailhe, Bull. Soc. Chim. (4) 29, 221 (1921) reports the boiling point of this compound as 176°.
- (6) Vosburgh and Cooper, J. Am. Chem. Soc., 63, 437 (1941)
- (7) See Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corporation, New York. p. 190 ff.
- (8) Taylor and Kraus, J. Am. Chem. Soc., 69, 1731 (1947).
- (9) Thompson and Kraus, J. Am. Chem. Soc., 69, 1016 (1947).
- (10) Tucker and Kraus, J. Am. Chem. Soc., 69, 454 (1947).
- (11) Reynolds and Kraus, J. Am. Chem. Soc., 70, 1709 (1948).
- (12) Kaplan, Hildebrandt, and Ader, ANL-4521
- (13) McLane, Dixon and Hindman, in "The Transuranium Elements, Research Papers," National Nuclear Energy Series, Division IV, Volume 14B, McGraw-Hill 1949, p. 358.
- (14) Ref. (7), p. 118.

FIG.1. ABSORPTION SPECTRA OF URANYL NITRATE IN SOME KETONIC SOLVENTS.

- 0.02 M URANYL NITRATE IN ACETONE
- 0.02 M URANYL NITRATE IN METHYL ISOBUTYL KETONE
- · - · - 0.02 M URANYL NITRATE IN CYCLOHEXANONE
- 0.02 M URANYL NITRATE, 0.02 M TETRABUTYLAMMONIUM NITRATE IN ACETONE.

FIG. 2. REACTION BETWEEN URANYL NITRATE AND TETRABUTYLAMMONIUM NITRATE IN METHYL ISOBUTYL KETONE.

○ 455 mμ
Δ 470 mμ