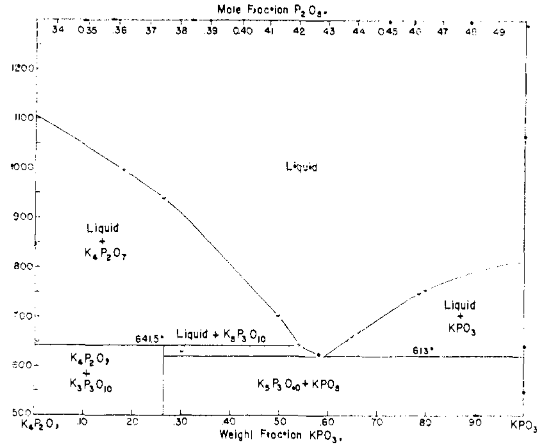

Fig. 2.—Phase equilibrium diagram of the binary system $K_4P_2O_7$–KPO_3.

TABLE IV

MELTING POINTS IN THE SYSTEM $K_4P_2O_7$–KPO_3

Wt. fraction KPO_3	Mole fraction P_2O_5	Liquidus temp., °C.	Primary phase
0	0.3333	1109	$K_4P_2O_7$
.1800	.3616	995	$K_4P_2O_7$
.2634	.3759	940	$K_4P_2O_7$
.4977	.4134	702	$K_4P_2O_7$
.5400	.4204	644	$K_4P_2O_7$
.5802	.4271	625	$K_5P_3P_{10}$
		613	Eutectic
.7986	.4645	754	KPO_3
1.0	.5	813	KPO_3

TABLE V

COMPOUNDS AND INVARIANT POINTS IN THE SYSTEM $K_4P_2O_7$–KPO_3

$K_5P_3O_{10} \rightleftarrows K_4P_2O_7 + L$; $t = 641.5°$; $L = 0.54$ wt. fraction KPO_3

$K_5P_3O_{10} + KPO_3 \rightleftarrows L$; $t = 613°$; $L = 0.59$ wt. fraction KPO_3

Compound	Sign	ω	ϵ	M.p., °C.
$K_4P_2O_7$	+	1.495	1.502	1105
$K_5P_3O_{10}$	−	1.520	1.516	
KPO_3	+	1.465	1.483	813

with formation of pyrophosphate and liquid. The reaction

$$K_5P_3O_{10} \rightleftarrows K_4P_2O_7 + L$$

takes place at 641.5°, and the liquid contains 0.54 weight fraction KPO_3, or, expressed in mole fraction K_2O and P_2O_5, 0.58 and 0.42. $K_5P_3O_{10}$ is the stable crystalline phase in contact with liquid from this invariant point to the eutectic with KPO_3 at 613°. At this invariant point the reaction

$$K_5P_3O_{10} + KPO_3 \rightleftarrows L$$

takes place, and the liquid contains 0.59 weight fraction KPO_3, or expressed in mole fractions K_2O and P_2O_5, 0.571 and 0.429. From this eutectic the melting point curve rises to the melting point of KPO_3, 813°, with KPO_3 as the stable crystalline phase.

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Polymerization of Uranyl–Citrate, –Malate, –Tartrate and –Lactate Complexes[1]

BY ISAAC FELDMAN, JEAN R. HAVILL AND W. F. NEUMAN

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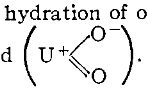
Titrimetric and spectrophotometric studies suggest the following conclusions: (1) When equimolar mixtures of uranyl nitrate and citric, tartaric, and malic acids are raised to *p*H 3.5, practically all the uranium reacts with the organic groups by tridentate chelation to form polynuclear complexes having a 1:1 molar ratio and held together by oxygen bridges or by hydroxyl bridges between uranium atoms. On the basis of previous polarographic evidence, the polymers are believed to be dimers. (2) At slightly alkaline *p*H these dimers react completely to form trinuclear complexes. There exist two trimers, having (uranium/organic group) ratios of *3:3* and *3:2*. The stability of the *3:3* trimer relative to the *3:2* trimer decreases in the order —UMal > UTar > UCit—probably due to electrostatic effects. It is believed that steric hindrance to linearity of the (O=U=O) group is produced by the tridentate chelation with either (a) an accompanying hydration of one of the originally double-bonded oxygens of the uranyl group or (b) formation of the bent resonance hybrid  $\left(U^{+}\begin{smallmatrix}O^{-}\\ O\end{smallmatrix}\right)$. Possible structures for the polymers are presented and discussed. Titration results also suggest dimerization and trimerization of the uranyl–lactate complex in an equimolar mixture.

The titrimetric and spectrophotometric studies reported here were carried out as part of a program of investigation of the reactions of uranyl ions with organic acids.[2] These studies have furnished information regarding the polymerization of complex ions formed by the reaction of uranyl ions with citrate, malate, tartrate and lactate ions.

Experimental

Materials.—The malonic, tricarballylic and l-malic acids were all Eastman White Label grade. Mallinckrodt U.S.P. sodium barbital was used. All other chemicals were C.P. grade. C.P. β-hydroxybutyric acid was obtained from Matheson Co. Distilled water was used for each solution. To avoid photochemical effects all solutions were prepared in semi-darkness and stored in the dark.

Methods.—Potentiometric titrations were carried out in a semi-dark room at room temperature with the aid of a Beckman Model G *p*H meter using external electrodes. Spectrophotometric measurements were made with a Beckman DU

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[1] This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester, Atomic Energy Project, Rochester, New York. Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Kansas City, Missouri, April, 1954.

[2] Previous papers in this series are: (a) I. Feldman and W. F. Neuman, THIS JOURNAL, **73**, 2312 (1951); (b) W. F. Neuman, J. R. Havill and I. Feldman, *ibid.*, **73**, 3593 (1951); (c) I. Feldman and J. R. Havill, *ibid.*, **76**, 2114 (1954).

spectrophotometer using 10-mm. Corex cells. Where indicated, mixtures were centrifuged for one hour at 40,000 × gravity in a Servall Model SS-2 Vacuum centrifuge.

Except where noted (Fig. 2), absorption spectra and continuous-variations curves are reported for mixtures which had been allowed to stand in the dark for about 48 hours, since 24–48 hours were required to insure constant results for mixtures in which precipitation occurred. Equilibrium, which was maintained for at least four days, was reached within 24 hours for all solutions in which precipitation did not occur.

Results and Discussion

In Fig. 1 are presented the titration curves of equimolar mixtures of uranyl nitrate and the several hydroxy carboxylic acids, lactic, malic, tartaric and citric. The uranyl–citrate (UCit), uranyl–malate (UMal) and uranyl–tartrate (UTar) curves have two striking features in common. (i) The first inflection point occurs near *p*H 3.5 when OH/U, the ratio of the number of moles of *added* base to the *total* number of gram atoms of uranium, is three. (ii) The second inflection point occurs in slightly alkaline solution when the OH/U ratio is equal to $1^2/_3$ plus the number of carboxyl groups in the original carboxylic acid; *i.e.*, at $3^2/_3$ for the UMal and UTar curves and $4^2/_3$ for the UCit curve. The ULact curve shows only one inflection point, at OH/U equal to $2^2/_3$.

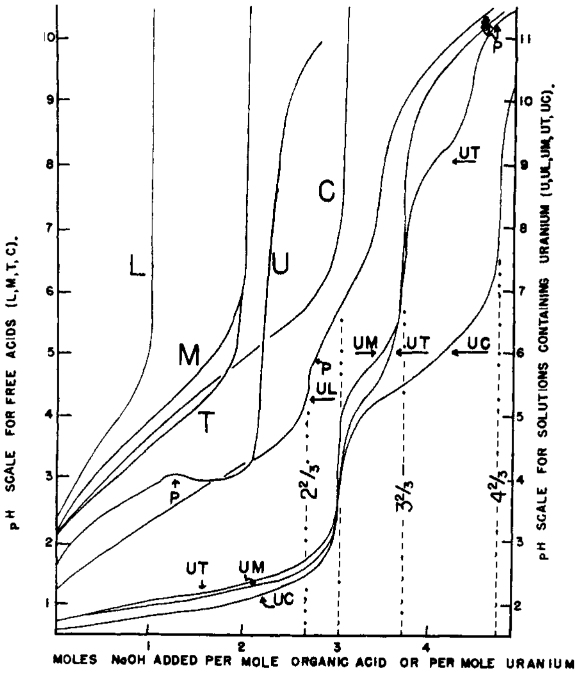
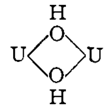


Fig. 1.—Titration of various organic acids, of uranyl nitrate, and of *equimolar* mixtures of these acids and uranyl nitrate: 100 ml. of each solution, which was 0.05 *M* in each of the indicated constituents was titrated with 0.863 *M* NaOH. Curves L, M, T and C are for titrations of lactic, malic, tartaric and citric acid, respectively; U represents the titration of uranyl nitrate; UL, UM, UT and UC represent titrations of *equimolar* mixtures of uranyl nitrate with lactic, malic, tartaric and citric acid, respectively. P indicates formation of a visible cloudiness (*i.e.*, precipitate).

Dimerization in Acid Solution.—In view of the previous polarographic evidence[2b] that the 1:1[3] UCit complex exists principally as a dimer up to *p*H 4.6 and since it is known from spectrophotometric studies[2a,c] that 1:1 stoichiometry predominates in equimolar mixtures of uranyl nitrate with citric, malic and tartaric acids in the *p*H range 3.5–4.5, it seems evident that the first inflection point at (OH/U = 3) is due to the formation of a dinuclear complex held together by either an oxygen bond, as in U–O–U, or by two hydroxyl bridges, as in



The concept of dimerization through an oxygen bond is suggested by the work of MacInnes and Longsworth[4] and of Sutton[5] who concluded that uranyl ions dimerize and trimerize in this manner. However, their results would also be consistent with polymerization through hydroxide bridges. This latter type of bonding has been shown to exist in the crystalline basic salts of Th(IV) and U(IV) by Lundgren and Sillen.[6]

Tridentate Character of the UCit, UMal and UTar Complexes in Acid Solution.—In Fig. 2 are presented the absorption spectra of mixtures of uranyl nitrate in 8-fold excess of various organic acids at *p*H 3.5 and at *p*H 4.5. It has been shown previously[2a,c] that at these *p*H's 1:1 stoichiometry predominates in the UCit, UMal, UTar and ULact systems. Although the stoichiometry in the other systems has not been established, the spectra of 1:1 uranyl–malonate and uranyl–tricarballylate mixtures are about 10% lower than the 1:9 spectra. The spectrum of a 1:1 β-hydroxybutyrate mixture was not obtained, because the β-hydroxybutyrate was not completely soluble and a misleading spectral curve would undoubtedly have resulted.

The UCit, UMal and UTar curves are quite similar to each other, but their unique contour is definitely different from the contours of the other curves. This indicates that below *p*H 4.5 the electronic structure of the uranium atoms is very similar in the UCit, UMal and UTar dimers but is very different from the electronic structure of uranium in complexes containing lactate, malonate, β-hydroxybutyrate or tricarballylate. The only electronic configuration which UCit, UMal and UTar could have in common which could not be present in one of the other complexes is the configuration due to the tridentate group composed of two carboxyl groups and one hydroxyl group.

Stoichiometry at Slightly Alkaline *p*H.—In Fig. 3 are presented the absorption spectra of a number of mixtures at *p*H 8. Three significant features may be noted: (1) For each system, when excess organic acid is present the spectrum has the

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(3) Throughout this paper a numerical ratio expressed in arabic numerals has *no significance* with regard to the polymeric state of a complex. On the other hand, a ratio expressed in italic numerals includes the actual number of uranium atoms and organic groups in one complex ion. That is, a 1:5 UCit mixture is prepared by mixing uranyl nitrate and citric acid in a 1:5 molar ratio; although this mixture contains 1:1 UCit complexes in both acid and basic solution, *2:2* UCit dimers are present in acid solution and *3:3* trimers are present in basic solution.

(4) D. A. MacInnes and L. G. Longsworth, Manhattan Project Report MDDC-911 (1942).

(5) J. Sutton, *J. Chem. Soc.*, Supplementary Issue No. 2, S275 (1949).

(6) G. Lundgren and L. G. Sillen, *Arkiv. Kemi*, **1**, 277 (1950); G. Lundgren, *ibid.*, **2**, 535 (1950); G. Lundgren, *ibid.*, **4**, 421 (1952).

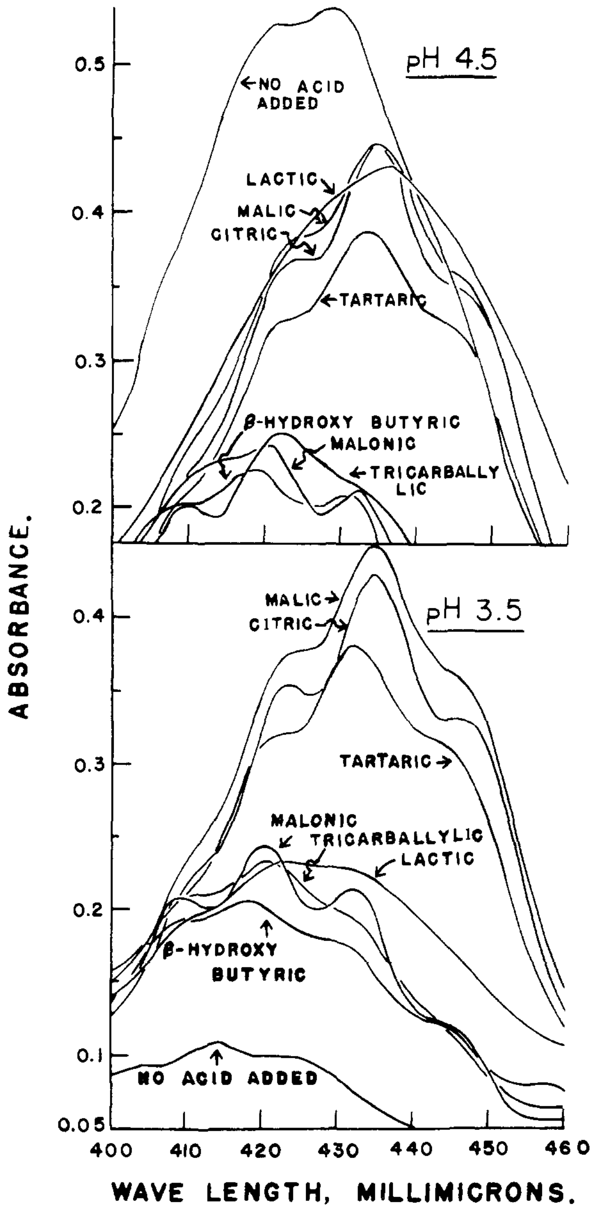

Fig. 2.—Absorption spectra of 1:9 mixtures of uranyl nitrate and various organic acids at *p*H 3.5 and at *p*H 4.5. Each solution was 0.01 *M* in uranyl nitrate and 0.09 *M* in organic acid. Associated with each curve is the name of the organic acid in the mixture studied. 0.1 *M* sodium perchlorate was present in the solution to which no acid was added.

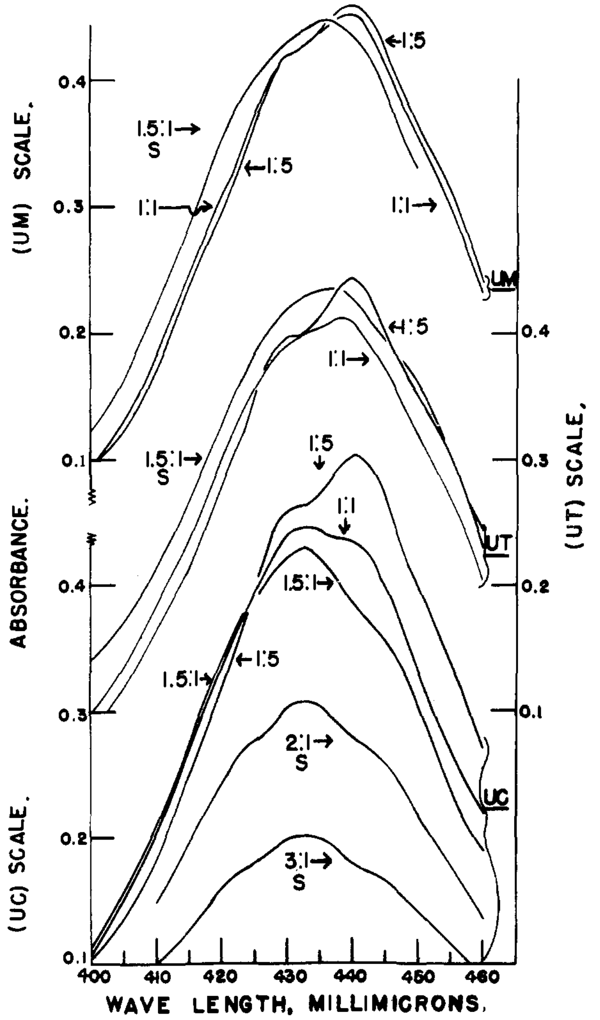

Fig. 3.—Absorption spectra of uranyl nitrate–organic acid mixtures at *p*H 8. *Each* solution contained 0.005 *M* uranyl nitrate. The numerical ratio associated with each spectrum represents the initial (uranium/organic acid) molar ratio of the solution studied. The letter S indicates that the spectrum was obtained for the supernatant liquid after the mixture had been centrifuged at 40,000 × gravity for one hour. Sodium barbital was added (0.025 *M*) to each solution to act as buffer. *p*H adjustments were made with droplets of sodium hydroxide. The symbols UM, UT and UC represent uranyl–malate, uranyl–tartrate and uranyl–citrate mixtures, respectively. Each spectrum was obtained about 48 hours after the mixture was prepared. Spectra of 1:12 mixtures were identical with the 1:5 curves.

same contour. There is a peak at 440 mμ and a shoulder at 431 mμ, the shoulder being 0.9 as high as the peak. (2) For the UMal system the spectrum of an equimolar mixture is only slightly different from the spectrum of a solution containing excess malate. (3) The spectra of equimolar UTar and UCit mixtures are quite different from the spectra of solutions containing excess anion. In fact, an equimolar UCit mixture has its spectral peak at 432 mμ.

These spectral features suggest that at slightly basic *p*H: (i) 1:1 stoichiometry predominates in the 1:1 UMal mixture and in all three systems—UMal. UTar and UCit—when excess organic anion is present; (ii) 1:1 UTar and UCit mixtures contain, in addition to some of the 1:1 complex, some complex containing a (uranium/organic anion) ratio greater than 1:1; and (iii) this latter complex (*i.e.*, > 1:1) is present to the greatest extent in the UCit system.

For the UCit system this latter complex (>1:1) appears to exhibit a 1.5:1 (uranium/organic anion) ratio, as a consideration of the spectral curves of the 1.5, 2:1 and 3:1 UCit mixtures of Fig. 3 will show. All three curves exhibit the same general contour and the same peaks and shoulders. Within experimental error, these curves differ only because of mass action; there is no evidence of a complex ion species of combining ratio higher than 1.5:1. Furthermore, since uranium did not precipitate from the 1.5:1 mixture, its spectrum can be considered the spectrum of the pure 1.5:1 complex. Assuming the spectra of the 1:5 and 1:12 mixtures to represent the spectrum of the pure 1:1 complex, the spectrum of the equimolar mixture can be accounted for. within experimental error, as a 60:40 mixture of the 1:1 and 1.5:1 species, respectively.

Spectra of the supernatant liquid of the UMal mixtures, 1.5:1, 2:1 and 3:1, were analogous to the UCit system; there was no evidence of the existence of a complex species having a combining ratio higher than 1.5:1.

The UTar system does show evidence of the presence of ion species of combining ratio higher than 1.5:1. The spectrum of the 1:1 UTar mixture does not lie between the spectra of the 1.5:1 and 1:5 mixtures, indicating the presence of ions of higher combining ratio even in the 1.5:1 mixture.

The above conclusions regarding stoichiometry were confirmed by the application of Job's well-known method of continuous variations.[2a,7,8] In Fig. 4A the existence of a very strong 1.5:1 UCit complex is shown by the very sharp peaks in the 420 and 432 mμ curves.

The existence of a 1:1 UCit complex is demonstrated by the maximum at $X = 0.5$ in the 365 mμ curve. The non-linearity of this curve from $X = 0.25$ to 0.5 shows, however, that the 1:1 complex is dissociated to some extent except in the presence of at least a 3-fold citrate excess. Even after centrifugation with a force of 40,000 × gravity for one hour, precipitation occurred only in those solutions for which $X > 0.6$. Therefore, in a 1.5:1 UCit mixture virtually all the uranium is in the 1.5:1 form. In fact, assuming that the 1:5 and 1.5:1 curves in Fig. 2 represent the spectra of undissociated 1:1 and 1.5:1 complexes at *p*H 8.4, one calculates from the actual and extrapolated peak values in the 365 mμ curves that in the 1:1 mixture used for the continuous-variations study 60% of the uranium was in the 1:1 form and 40% was in the 1.5:1 form. This is the same value calculated previously from the 435–460 mμ portions of the absorption spectra.

The results of the application of the method of continuous variations to the UTar system are given in Fig. 4B. Though the absorption spectra, above. indicate the existence of a 1:1 complex ion, this species could not be demonstrated by the continuous-variations method presumably because the absorptivity requirements[9] were not met at any wave length between 350 and 500 mμ. The existence of the 1.5:1 complex was clearly evident from the peaks at $X = 0.6$, Fig. 4B. There was also an indication of complexes having combining ratios higher than 1.5:1, but the data in the region of the shoulders, $X = 0.75$, are not reproducible, probably due to difficulties in the removal of the gelatinous precipitate of uranium.

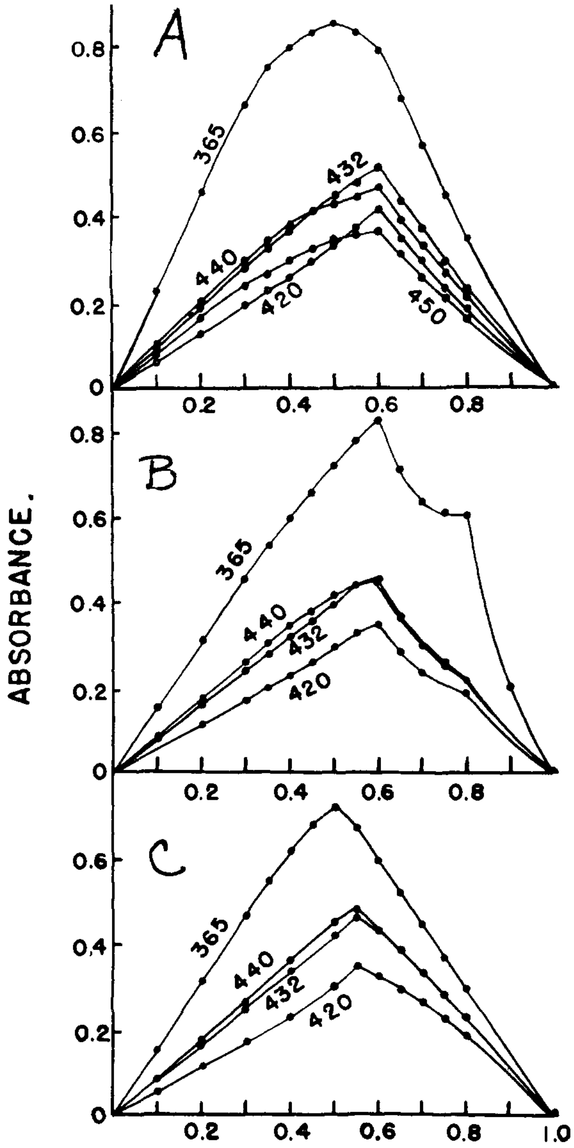

Fig. 4.—Method of continuous-variations applied to (A) uranyl–citrate system at *p*H 8.5; (B) uranyl–malate system at *p*H 7.5; (C) uranyl–tartrate system at *p*H 7.5. The initial (UO_2^{++} + organic acid) was 0.01 *M* in each solution. Sodium barbital was added (0.025 *M*) to each solution to act as buffer. Each solution contained 0.075 *M* sodium perchlorate. Abscissa X represents the initial molar ratio (UO_2^{++}/UO_2^{++} + organic acid). The number associated with each curve is the wave length in millimicrons at which absorbance was measured. Each mixture was centrifuged at 40,000 × gravity for one hour and the absorbance of the supernatant liquid was measured. *p*H adjustments were made with droplets of sodium hydroxide.

The UMal continuous-variations studies are represented by Fig. 4C. The peak at $X = 0.5$ in the 365 curve for *p*H 7.5 shows the existence of a 1:1 complex at this *p*H. However, since this peak is about 7% lower than the extrapolated peak and since at this *p*H no precipitation occurred in mixtures for which $X \leqq 0.55$ even after centrifugation

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(7) P. Job, *Ann. Chim.*, **11**, 97 (1936).

(8) W. C. Vosburgh and G. R. Cooper, THIS JOURNAL, **63**, 436 (1941).

(9) The absorbance per gram-atom of uranium of the 1:1 complex must be greater than 1.2 times that of the 1.5:1 complex. See A. L. Underwood, T. Y. Toribara and W. F. Neuman, *ibid.*, **72**, 5597 (1950).

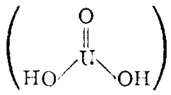
at 40,000 × gravity for one hour. there is also present in a 1:1 UMal mixture a small amount of another soluble complex.

The latter complex has a (U/Mal) ratio of 1.5:1. This conclusion results from the UMal absorption spectra studies discussed above and from the fact that the 1.5:1 complex was clearly demonstrated for the UCit and UTar system. Peaks were obtained at $X = 0.55$, rather than at $X = 0.6$, for the other wave lengths because the stability of the 1:1 complex relative to the 1.5:1 complex is greater in the UMal system than in the UCit or UTar systems. Thus, in a UMal mixture having ($X = 0.55$) there is sufficient malate to complex in the 1:1 form any uranium not held in the 1.5:1 form. This is not true, however, in a 1.5:1 mixture. When $X = 0.6$ sufficient uranium is taken out of solution by precipitation to cause the spectral absorbance of the supernatant liquid to fall below that of a mixture having ($X = 0.55$) at any wave length.

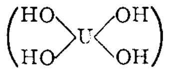
This latter phenomenon does not occur in the UCit and UTar systems. In these systems the ratio of the stability of the 1:1 complex to that of the 1.5:1 form is not great enough to cause the amount of precipitation of uranium necessary to produce the phenomenon. However, the appearance of some precipitate in a 1.5:1 UTar mixture indicates the ratio of the stability of the 1:1 complex to that of the 1.5:1 form is greater for the UTar system than for the UCit system.

Effect of Chelation on Uranyl Group.—A study of a Fisher–Hirschfelder–Taylor molecular model shows that tridentate binding of uranium by a hydroxy dicarboxylic acid would probably produce significant steric hindrance and electrostatic repulsion to the 180° bond angle of the uranyl grouping. The linearity of the uranyl entity may be destroyed by hydration of one or both of the oxygens to give

(a)

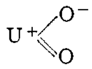


or (b)



or by a transition to the bent resonance hybrid

(c)



The occurrence of grouping (b) in the tridentate UCit, UMal or UTar complex is believed to be the least likely because of steric factors. Considering the three bonds resulting from tridentate chelation and at least one bond from dimerization, the presence of the $U(OH)_4$ group would require that eight oxygen atoms be bonded to each uranium. Since the ionic-radius ratio of U^{+6} to O^{-2} (or to OH^-), 0.83/1.45 or 0.57, is significantly smaller than 0.65, the minimum radius ratio limit[10] for coördination number eight, it would be expected that eight oxygen atoms could be bonded to uranium only under optimum conditions. Such conditions should not prevail in the tridentate groups because the three bonded oxygens cannot occupy the minimum space for three oxygens around the uranium without introducing strain into the chelate rings. Furthermore, since the steric factors do not require that both (U=O) bonds be broken, the natural tendency to preserve this double bond should make group (b) the least stable.

The *2:2* Dimer.—Four structures which are consistent with the above results and discussions may be written for the *2:2* dimer at *p*H 3.5–4.5. These structures are represented by formulas I through IV in Table I. For any of these structures, the *2:2* dimer would bear a charge of −2. In view of the weakly acidic nature of alcoholic hydrogens, the probability seems small that dimer structures lacking alcoholic hydrogen atoms need to be considered below *p*H 4.5.

The *3:3* Trimer.—The titration curve of a 1:5 UCit mixture (curve 1, Fig. 5) contains only one inflection point, at an OH/U ratio equal to $16^2/_3$ at about *p*H 8.5. The titration of a 1:5 UTar mixture, represented by curve 2 of Fig. 5, shows one inflection point at OH/U equal to $11^2/_3$ near *p*H 8.5 and a second inflection point at OH/U equal to about $12^1/_3$ near *p*H 10.5.

For the 1:5 uranyl–malate mixture a titration curve obtained in the usual manner, instead of having only one inflection point in slightly basic solution, actually contains two inflection points in the *p*H range 7–9.5. As seen in curve 3, Fig. 5, the first point occurs near *p*H 7 and has an OH/U ratio equal to about 11; the second point has an OH/U ratio equal to $11^2/_3$ near *p*H 9.5. The first inflection point occurs because in the presence of excess malate the rate of reaction in basic solution is a function of *p*H.

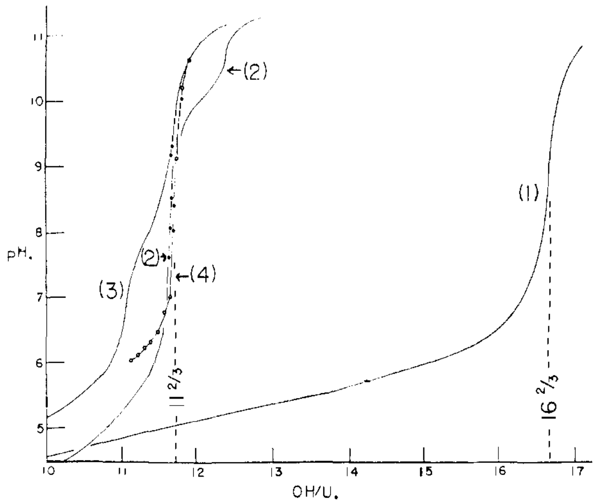


Fig. 5.—Titration of 1:5 uranyl nitrate–organic acid mixtures. Curves 1, 2 and 3 represent conventional potentiometric titrations of 1:5 UCit, UTar and UMal mixtures, respectively: 25.0 ml. of each mixture, initially 0.04 *M* in uranyl nitrate and 0.20 *M* in malic acid, was titrated with 0.854 *M* sodium hydroxide. Curve 4 was obtained as follows: To a series of 25.0-ml. volumes of solution, 0.04 *M* in uranyl nitrate and 0.04 *M* in malic acid, were added quantities of 0.854 *M* sodium hydroxide varying from 13.0 to 13.9 ml. The OH/U ratio was thus varied from 11.1 to 11.9. The equilibrium *p*H values (*i.e.*, constant values obtained within 12–24 hours) are plotted as the circles of which curve 4 is composed.

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[10] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 244.

The points of curve 4, Fig. 5, were obtained by measuring the *p*H as a function of time for a series of 1:5 uranyl–malate mixtures to which had been added the quantities of sodium hydroxide necessary to give OH/U ratios ranging from 11.1 to 11.9. Constant *p*H was obtained for each solution within 24 hours. The spectrum of a 1:5 UMal mixture in barbiturate buffer at *p*H 7.5 undergoes a general increase in height of about 25% during the first 24 hours after preparation of the solution. After 24 hours the spectrum of this mixture is identical with that of a 1:5 mixture at *p*H 9, the latter spectrum being independent of time. From curve 4 it is obvious that, when equilibrium systems are considered, there is only one inflection point in the (*p*H *vs.* OH/U) curve for a 1:5 UMal mixture and that this point is at OH/U equal to $11^2/_3$.

The integers (16, 11 and 11) in the OH/U ratios for the first inflection points in curves 1, 2 and 4 of Fig. 5 can be completely accounted for by assuming complete neutralization of all the carboxylic hydrogens, the alcoholic hydrogens of the malic and citric acid, and only one of the alcoholic hydrogens in tartaric acid. Curves C, T and M of Fig. 1 demonstrate that all the carboxylic hydrogens are neutralized by *p*H 7.5. The second inflection point near *p*H 10.5 in curve 2 undoubtedly represents the same reaction as does the third inflection point near *p*H 10.5 in the titration curve for the 1:1 UTar mixture. Since this inflection point does not occur in the UMal and UCit titration curves, it is most likely due to the removal of the second alcoholic hydrogen of the tartrate grouping and is evidence that the reaction responsible for the inflection point near *p*H 8.5 in each of the three systems involves the removal of one alcoholic hydrogen per organic group.

These conclusions are consistent with the same type of tridentate chelations (*i.e.*, involving two carboxyls plus one alcoholic oxygen) which is believed to prevail below *p*H 4.5. At alkaline *p*H, the spectra of 1:1 UCit, UMal and UTar complexes (*i.e.*, of 1:5 mixtures) are quite similar to each other but are different from the spectra observed for acid solutions. The alkaline spectra would be expected to be different from the acid spectra if the alcoholic hydrogens ionize at basic *p*H. Further evidence for tridentate chelation in basic solution is the relatively great stability of 1:1 UMal, UTar and UCit solutions. In 1:1 ULact, UMalonate and UTricarballylate mixtures and in a 1:10 uranyl-β-hydroxybutyrate mixture the uranium begins to precipitate by *p*H 6. In 1:1 UCit, UMal and UTar mixtures, however, precipitation does not begin until above *p*H 11.

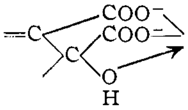
Since 1:5 UMal, UTar and UCit mixtures are composed of 1:1 complexes plus 4-fold excess organic anion, the most reasonable explanation for the fraction, $^2/_3$, which occurs in the inflection points near *p*H 8.5 is that it is due to a transformation from the *2:2* dimer to a *3:3* trimer (*i.e.*, containing three uranium atoms and three organic groups), with two hydroxyl ions being required for the reaction. The formation of a *3:3* UCit, UMal or UTar trimer from three uranyl ions and three of the corresponding organic acid molecules thus requires 14, 11 and 11 hydroxyl ions, respectively.

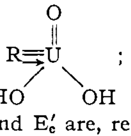
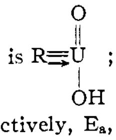
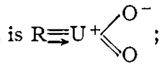
Molecular models indicate that, although seven oxygen atoms may group around each of the end uranium atoms without large steric strain, it is very unlikely that a *3:3* trimer can exist with more than six oxygens attached to the central uranium atom. It is possible to formulate only two structures for the *3:3* trimer which satisfy the stoichiometric

TABLE I

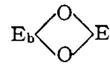
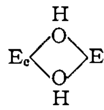
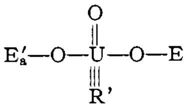
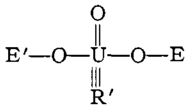
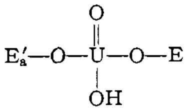
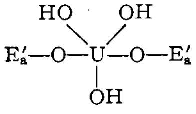
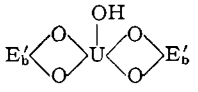
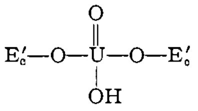
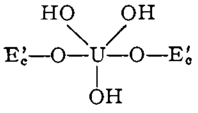
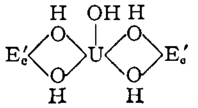
PLAUSIBLE STRUCTURES FOR UMal, UCit AND UTar COMPLEXES

Abbreviations used in Table I:

R is  ; R′ is R minus alcoholic hydrogen;

E_a is  $R\equiv\overset{\overset{O}{\|}}{\underset{HO\quad OH}{U}}$; E_b is  $R\equiv\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{U}}$; E_c is  ;

E'_a, E'_b and E'_c are, respectively, E_a, E_b, and E_c minus one alcoholic hydrogen atom.

Polymer represented	Plausible structures	Reference symbol
2:2 dimer	$E_a{-}O{-}E_a$	I
2:2 dimer		II
2:2 dimer	$E_c{-}O{-}E_c$	III
2:2 dimer		IV
3:3 trimer	 $E'_a{-}O{-}\underset{\underset{R'}{\vert\vert\vert}}{\overset{\overset{O}{\|}}{U}}{-}O{-}E$	V
3:3 trimer	 $E'{-}O{-}\underset{\underset{R'}{\vert\vert\vert}}{\overset{\overset{O}{\|}}{U}}{-}O{-}E$	VI
3:2 trimer	 $E'_a{-}O{-}\underset{\underset{OH}{\vert}}{\overset{\overset{O}{\|}}{U}}{-}O{-}E$	VIIa
3:2 trimer	 $E'_a{-}O{-}\underset{\underset{OH}{\vert}}{\overset{HO\quad OH}{U}}{-}O{-}E'_a$	VIIb
3:2 trimer		VIII
3:2 trimer	 $E'_c{-}O{-}\underset{\underset{OH}{\vert}}{\overset{\overset{O}{\|}}{U}}{-}O{-}E'_c$	IXa
3:2 trimer	 $E'_c{-}O{-}\underset{\underset{OH}{\vert}}{\overset{HO\quad OH}{U}}{-}O{-}E'_c$	IXb
3:2 trimer		X

requirements and the steric limitations. These structures are represented by formulas V and VI in Table I. According to either structure, the *3:3* UCit, UMal and UTar trimers would have charges of -8, -5 and -5, respectively.

The *3:2* Trimer.—The most reasonable view of the 1.5:1 complexes, revealed by the spectrophotometric results, is that they are trinuclear, containing three uranium atoms and two organic groups; *i.e.*, they are *3:2* trimers.

A titration curve of a 1.5:1 UCit mixture has its second inflection point at about *p*H 8 where the OH/U ratio is equal to $3^2/_3$. Since spectrophotometric studies showed that this mixture was composed almost entirely of the 1.5:1 complex, it is obvious that the formation of *3:2* trimer from three uranyl ions and two citric acid molecules required eleven hydroxyl ions.

Six plausible structures, represented by formulas VII through X in Table I, can be written for the *3:2* UCit trimer. In view of the resistance of (U=O) bonds to mere hydration, it is believed that structures VIIb and IXb are improbable since they are merely the hydrated forms of VIIa and IXa. The *3:2* UCit trimer would thus bear a -5 charge.

Titrations of 1.5:1 UTar and UMal mixtures did not yield definite inflection points, a fact undoubtedly connected with the precipitation noticed in these mixtures. If one assumes, however, that *3:2* UTar and UMal trimers are similar in structure to the *3:2* UCit trimer, then nine hydroxyl ions would be required for the formation of one *3:2* UMal or UTar trimer from three uranyl ions and two organic acid molecules. Such *3:2* UMal and UTar trimers would each have a -3 charge.

Relative Stabilities of *3:3* and *3:2* Trimers.—The stoichiometry indicates that the equilibrium between *3:3* and *3:2* trimers can be represented as

$$1 \text{ mole } 3{:}3 \text{ trimer} \rightleftarrows 1 \text{ mole } 3{:}2 \text{ trimer} + 1 \text{ mole anion, R}$$

The forward reaction involves the replacement of an organic R′ group by a hydroxyl ion, but the R′ ion immediately attaches a hydrogen ion, reforming the original alcohol group, to produce the free anion, R. Therefore, the hydroxyl ion does not enter the over-all stoichiometric equation.

This is the reason that the second inflection point in the titration curve of 1:1 mixtures (Fig. 1) occurs when OH/U equals $1^2/_3$ plus the number of carboxyl groups in the original carboxylic acid regardless of the fact that the ratio of *3:3* trimer to *3:2* trimer varies in the three systems studied, UCit. UMal and UTar.

The previously mentioned fact that the ratio of the stability of the 1:1 complex to the 1.5:1 complex at slightly alkaline *p*H decreases in the order UMal > UTar > UCit might suggest that the relative stability of *3:3* and *3:2* trimers depends on the size of the R′ group on the central uranium atom in the *3:3* trimer. However, molecular models indicate that the extra (CH_2COO^-) group of the citrate groups do not add a considerable amount of steric hindrance to that already existing in *3:3* UMal and UTar complexes. It is more likely that electrostatic repulsions by the (CH_2COO^-) groups are responsible for the stability differences. The reason for the time factor in the titration of a 1:5 UMal mixture (see Fig. 5) is not evident at present.

Uranyl–Lactate System.—The occurrence of the inflection point at OH/U = $2^2/_3$ near *p*H 6, just before precipitation occurs, in the titration curve of the 1:1 uranyl–lactate mixture may be considered evidence for the formation of a ULact trimer in the light of the previous interpretation of the factor, $^2/_3$. This, of course. implies the previous formation of dimer. However, the failure to obtain a titration break at OH/U = 2 suggests that trimer formation begins before dimer formation is complete.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY AND THE DEPARTMENT OF CHEMISTRY OF HARVARD UNIVERSITY]

The Chlorination of Metals in the Presence of a Donor Solvent[1]

BY ROBERT C. OSTHOFF AND ROBERT C. WEST

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A method for the low temperature chlorination of cobalt, nickel, manganese, zinc and chromium, in several donor solvents, is described. Several methods for the isolation of relatively pure anhydrous metal halides or coördination compounds of the anhydrous halides have been established. It is shown that the halogenation of the metals in the presence of donor solvents is a rather general one; and that it must involve coördination of the solvent to the metal, for these reactions do not occur in non-polar solvents.

I. Introduction

Pure anhydrous chlorides of metals are customarily prepared by passing chlorine gas over the pure metals at elevated temperatures,[2] since the procedure of drying the hydrated chlorides ordinarily leads to a certain amount of hydrolysis and loss of chlorine. This procedure is in certain cases unsatisfactory; for example, cobalt(II) chloride cannot be conveniently prepared in this way since it does not sublime appreciably at 500°, and the cobalt surface merely becomes covered with the chloride and the reaction ceases. However, iron(III)

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[1] Presented before the Division of Physical and Inorganic Chemistry, 125th Meeting of the American Chemical Society, Kansas City, Mo., March, 1954.

[2] L. Vanino, "Handbuch der Präparativen Chemie," Vol. I, Edwards Bros., Ann Arbor, Mich., 1943, pp. 489, 494, 544, 594 ff.