[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

Evidence of Polymerization in Titanium(IV) Sulfate Solutions

BY RICHARD E. REEVES AND FLORINE A. BLOUIN

RECEIVED MAY 21, 1954

Freshly prepared aqueous solutions of titanium sulfate, unlike titanium tetrachloride solutions, undergo rapid changes upon aging which are reflected in their behavior with tartaric acid. These changes are explained as due to the formation of dimers, or soluble short chain linear polymers, containing bidentate oxo bridges between titanium atoms. The occurrence of this type of polymerization preceding the precipitation of hydrated titanium dioxide from solution may be the reason for the production of the anatase crystal lattice, instead of the rutile lattice, upon the hydrolysis of solutions of titanium sulfate.

During studies of the reaction of titanium(IV) salts with cellulose and with simpler organic molecules in developing cotton flameproofing processes differences were observed in the behavior of titanium tetrachloride and titanium(IV) sulfate solutions which warranted further investigation. Although numerous studies[2–5] had already been made on the titanium tartrate complexes without reaching a complete understanding of the reactions involved, these complexes appeared to offer the best means for studying the observed differences between the chloride and sulfate solutions. The results of this investigation appear to cast new light upon the behavior of aqueous solutions of titanium sulfate.

Experimental

Stock solutions containing 0.5 mole of titanium per liter were prepared by adding tetraisopropyl titanate (TPT) to the calculated amount of chilled hydrochloric or sulfuric acid. The resulting solutions contained 2 moles of isopropyl alcohol and 0.5 mole of titanium tetrachloride, or titanium(IV) sulfate per liter. When freshly prepared these solutions were opalescent, but they became clear on standing in an ice-bath. One-half molar tartaric acid solutions were prepared from pure L-(+)-tartaric acid.

Continuous variation experiments were carried out at 27 ± 2° under two sets of conditions. (A) By adding X ml. of tartaric acid solution to 10 − X ml. of titanium salt solutions and observing the optical rotation in a one-dm. cell within 2 to 5 minutes after mixing. (B) By adding 10 ml. of 5 N ammonia to the solutions prepared under conditions A, and observing the optical rotations within 2 to 5 minutes after mixing. The difference between the observed rotations and those calculated for the tartaric acid alone, if no complexing had occurred, was plotted as the Y-coördinate against X, the ml. of tartaric acid solution.

Kinetic experiments upon the aging of titanium sulfate solutions were conducted at the titanium-to-tartrate ratio of 1:3. In these experiments the titanium sulfate solutions were prepared in freezing-baths with vigorous shaking in order to obtain clear solutions in the minimum time. The solutions then were brought rapidly to the desired temperature in a water-bath, and samples were withdrawn for reaction with tartaric acid. The rotations were observed within 2 to 5 minutes after mixing, and a series of similar observations were made after aging the titanium sulfate solutions.

Discussion

The continuous variation curves for tartaric acid *versus* titanium salt solutions are shown in Figs. 1 and 2. The upper curve in each figure represents the behavior of titanium tetrachloride solutions. Evidently in the acid solutions titanium tetrachloride forms a 1:2 complex with tartaric acid while in the ammoniacal solution a 1:1 complex is formed. The curves for titanium tetrachloride solutions were the same whether the solutions were freshly prepared or aged, provided that the aging had not proceeded so far that precipitation of titanium dioxide had occurred.

The lower curves of Figs. 1 and 2 represent the behavior of variously aged titanium sulfate solutions. In the acid solutions represented in Fig. 1 the peak of curves B and C corresponded to a titanium:tartrate ratio of 1:3 for the titanium sulfate solutions, while in the ammoniacal solutions the ratio was 1:1. A possible explanation for the difference between the ratio of reactants in the acid solutions containing chloride and sulfate will be advanced below. At this point attention is directed toward the observation that the position of the titanium sulfate curves is strongly dependent upon the time of aging of the titanium sulfate solutions. In Fig. 1, curve B was obtained from a solution which had been allowed to age for only 30 to 60 minutes at room temperature, while curve C was obtained from a titanium sulfate solution which had been aged for several days at 19.4°. In Fig. 2, curve B represents a titanium sulfate solution which was prepared immediately before the observations were made. Curve C represents the same solution after one hour aging at 19.4°, and curve D represents a titanium sulfate solution which had been aged for two days at room temperature.

The results of this work indicated that titanium tetrachloride solutions retain their initial reactivity toward tartaric acid as long as the solutions remained clear but that titanium sulfate solutions changed markedly with age. That this aging of titanium sulfate is accelerated by increasing temperatures is shown by the curves of Fig. 3. At the temperatures represented in this figure (19.4, 29.4, 50 and 60°) the optical rotations obtained by mixing the titanium sulfate solution with three volumes of tartaric acid decrease sharply with time and appear to approach minimum values which are lower the higher the temperature of aging. The titanium sulfate solutions remained clear throughout the experiments at the three lowest temperatures, but in the 60° experiment precipitation occurred at the point noted in the figure.

By regarding the point at which the tartaric acid rotations level off at the completion of the aging reaction it was calculated that the aging reaction obeys second-order kinetics at 19.4 and 29.4°. This might be regarded as indicative of the formation of a dimer in these solutions; however, we are not inclined to dismiss the possibility of the existence of other low molecular weight species. The absence

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[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

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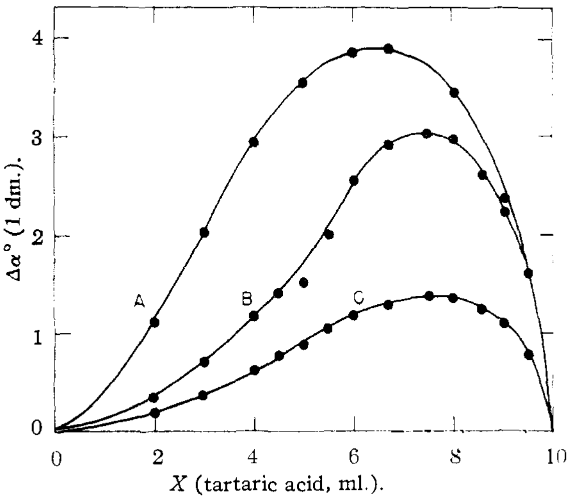


Fig. 1.—Continuous variation curves for tartaric acid *vs.* titanium salt solutions; X ml. of 0.5 molar tartaric acid was added to $10 - X$ ml. of 0.5 molar titanium salt: Curve A, $TiCl_4$; curves B and C, $Ti(SO_4)_2$.

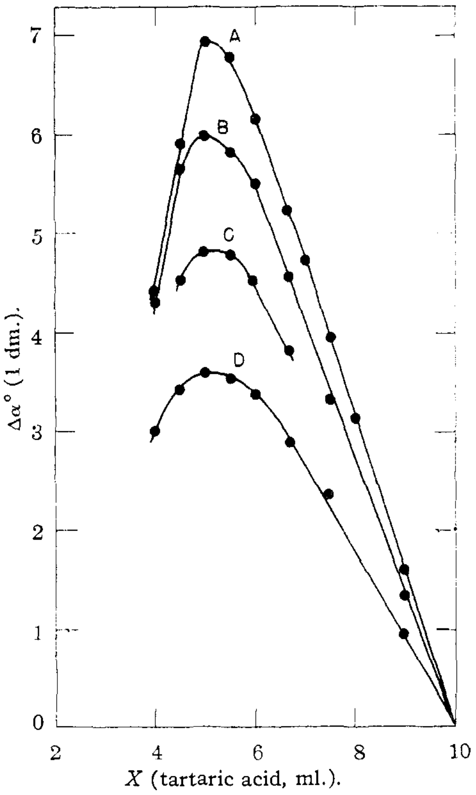


Fig. 2.—Continuous variation curves for tartaric acid *vs.* titanium salt solutions in the presence of excess ammonia; X ml. of 0.5 molar tartaric acid was added to $10 -$ X ml. of 0.5 molar titanium salt after which 10 ml. of 5 N ammonia was added: Curve A, $TiCl_4$; curves B, C and D, $Ti(SO_4)_2$.

of turbidity or of increased viscosity in these aged solutions is evidence against the presence of cross-linked, or long chain polymers.

Our interpretation of these results is that there is a type of polymerization which occurs in the presence of sulfate but not in the presence of chloride

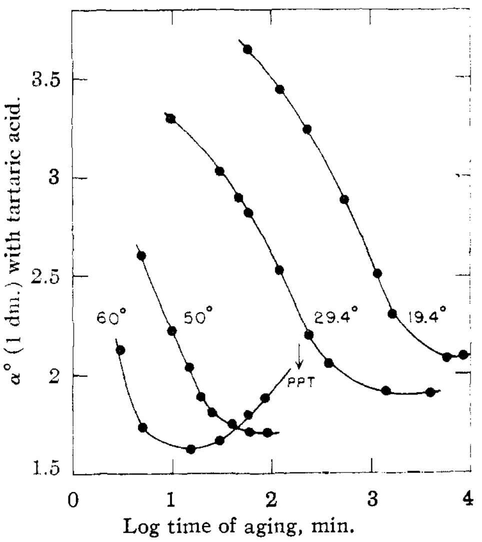
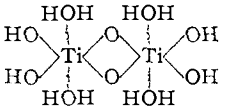


Fig. 3.—Optical rotations obtained by mixing titanium sulfate solutions aged for different periods and at different temperatures with tartaric acid. The tartaric acid–titanium ratio was 3:1. If no complexing had occurred the rotation due to the tartaric acid alone should have been 0.76°.

anion. In this type of polymerization it seems probable that dimers(I) or soluble, low molecular weight polymers(II) are formed containing bidentate oxo bridges.



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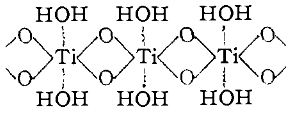

II

Only linear polymers are likely to occur with this type of bidentate linkage between titanium atoms; therefore this type of polymerization leads to a loss of chemical reactivity, but not to the formation of an insoluble precipitate.

The failure of this type of polymerization to occur in the presence of chloride ion is attributed to complexing between titanium and chloride. In this case the solution probably contains species of the general formula $H_2TiCl_n(OH)_{6-n}$, where $n < 4$. As long as n is appreciably greater than zero the opportunity for the formation of bidentate oxo bridges between two titanium atoms will be greatly reduced, hence the linear type of polymerization will not be favored in titanium tetrachloride solutions. Complexing with chloride would also explain the observation that in acid solution the titanium:tartrate combining ratio is lower for the chloride than for the sulfate.

Upon aging titanium sulfate solutions at 60° the initial decrease in reactivity with tartaric acid (as evidenced by the magnitude of the rotational effect) occurred very rapidly, and was followed by a slow increase in the rotation. This latter effect, evident in the 60° curve of Fig. 3, was still more pronounced at higher temperatures. At 70 and 90° the rotations showed a very rapid decrease to approximately 1.70°, after which the rotations increased. Not until the rotations had passed a minimum value and increased to about 2.10° was cloudiness or precipitation of hydrated titanium dioxide observed. This inflection appears to signify some change in polymeric structure preceding the precipitation of hydrated titanium dioxide from titanium sulfate solutions.

In the economically important hydrolyses of titanium salt solutions to produce titanium dioxide, titanium chloride solutions yield rutile while sulfate solutions produce anatase. Since the titanium tetrachloride solutions do not suffer any change in reactivity with tartaric acid until precipitation occurs while the sulfate solutions undergo pronounced changes in reactivity prior to their precipitation it appears reasonable to suppose that this difference in behavior may be related in some way to the ultimate formation of different types of crystal structures. The cross-linkage of linear titanic acid polymers such as are illustrated in diagram II may produce a different type of crystal lattice from that built up directly from the monomeric hydrated titanium chloride complexes.

NEW ORLEANS, LOUISIANA

[CONTRIBUTION FROM LOS ALAMOS SCIENTIFIC LABORATORY, UNIVERSITY OF CALIFORNIA AND UNIVERSITY OF CHICAGO]

Preparation, Identification and Crystal Structure of a Pentavalent Americium Compound, $KAmO_2F_2$[1]

BY L. B. ASPREY, F. H. ELLINGER AND W. H. ZACHARIASEN[2]

RECEIVED MARCH 15, 1954

$KAmO_2F_2$, prepared by the addition of a saturated solution of KF to an acid solution of pentavalent americium, is rhombohedral, $R\bar{3}m$, with one molecule in a unit cell with $a = 6.78$ Å., $\alpha = 36.25°$. The atomic positions are: 1 Am in (0,0,0), 1 K in ($^1/_2$,$^1/_2$,$^1/_2$), 2 O in $\pm$ (u,u,u) with $u = 0.102$, 2 F in $\pm$ (v,v,v) with $v = 0.356$. The structure ($CaUO_2O_2$ type) contains radicals $[AmO_2]^+$ and is built up of layers $(AmO_2F_2)^-$ held together by potassium ions.

The preparation of double carbonates of alkali with pentavalent transuranic elements was recently described by Nigon, *et al.*[3] The crystal structure of the hexagonal double carbonates has been determined for the isostructural series: $KPuO_2CO_3$, $NH_4PuO_2CO_3$ and $RbAmO_2CO_3$.[4] The present paper gives the results of X-ray diffraction studies of the double fluorides.

Preparation of the Compounds.—The americium used in this study contained no impurities above the spectroscopic limit of detection.

$KAmO_2CO_3$ was prepared by OCl^- oxidation of Am(III) in K_2CO_3 solution[3,5]; $RbAmO_2CO_3$ was prepared by $S_2O_8^{--}$ oxidation of Am(III) in Rb_2CO_3 solution.[3]

The alkali Am(V) carbonate compounds were washed with dilute alkali carbonate solution to reduce alkali carbonate concentration to <0.1 *M* $CO_3^=$ and to remove other ions. The solids were then dissolved in dilute HNO_3 to give a solution of AmO_2^+ in <0.1 *M* H^+.

The solution, containing approximately 10–20 g./l. of AmO_2^+, was treated with an equal volume of saturated alkali fluoride. The white precipitate formed was allowed to stand for 5–10 minutes, washed three times with *ca.* 10 volumes of water per wash, and slurried into a capillary. The solid, containing ~30 micrograms of americium,[6] was centrifuged into the capillary tip and the supernatant removed by means of a smaller capillary inserted into the larger one. The solid was then washed once with acetone, air-dried, and sealed off preparatory to X-ray examination.

X-Ray Diffraction Data and Chemical Composition.—The investigation is based upon two different samples, one being a potassium–americium fluoride precipitate, and the other an analogous preparation made with rubidium instead of potassium. It was subsequently found that the commercially supplied rubidium salt which was used in making the latter sample contained considerable amounts of potassium.

The X-ray diffraction data obtained with CuKα radiation for the pure potassium preparation (Table I) can be ascribed to a single phase with a rhombohedral unit cell of dimensions[7]: $a = 6.78 \pm 0.01$ Å., $\alpha = 36.25 \pm 0.05°$. The second sample, the rubidium preparation made with appreciable potassium content, gave unit cell dimensions: $a = 7.03 \pm 0.01$ Å., $\alpha = 35.11 \pm 0.05°$. The sample was found to contain a small amount of rubidium silicofluoride and traces of an unknown phase. The considerable increase in cell dimensions of the second sample over the first is proof that the alkali atoms are constituents of the structure. In view of the impure nature of the second sample, the crystal structure determination is based upon the diffraction data of the pure potassium preparation.

According to the method of chemical preparation, the cation constituents of the structure are K^+ and Am(V). It is generally supposed, and indeed directly verified for the double carbonates,[3] that the pentavalent state of americium involves radicals $[AmO_2]^+$. The conceivable anion constituents other than the oxygen atoms of the possible radicals $[AmO_2]^+$ are fluoride and nitrate ions.

It has been amply demonstrated for compounds of the heavy elements that it is possible to assign fixed volume requirements to the various ions, V_i, so that the volume of the unit cell is given (usually to better than 5%) by the sum ΣV_i.[8] Small, highly charged cations like Am^{+5} and N^{+5} have negligible volume requirements, since they fit into the interstices between the anions; others have assigned

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[1] This work was sponsored by the U. S. Atomic Energy Commission.

[2] Consultant to Los Alamos Scientific Laboratory; present address, University of Chicago, Chicago, Illinois.

[3] J. P. Nigon, R. A. Penneman, E. Staritzky, T. K. Keenan and L. B. Asprey, *J. Phys. Chem.*, **58**, 403 (1954).

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[5] L. B. Werner and I. Perlman, THIS JOURNAL, **73**, 495 (1951).

[6] Excessive film blackening results from the γ-radiation of Am^{241} with larger amounts of sample.

[7] The hexagonal cell has dimensions $a_1 = 4.22$ Å. $a_3 = 18.99$ Å.

[8] See, for instance W. H. Zachariasen, THIS JOURNAL, **70**, 2147 (1948).