

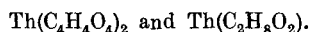
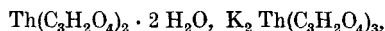
A Study on Thorium Compounds of some Dicarboxylic Acids

R. C. AGGARWAL, T. N. SRIVASTAVA and S. P. AGRAWAL

With 3 Figures

Summary

From solutions of $\text{Th}(\text{NO}_3)_4$ and K_2X ($\text{X} =$ malonate, succinate and adipate) taken in different molar ratios, the following compounds were isolated:



Conductometric and heterometric titrations carried out in the systems $\text{Th}(\text{NO}_3)_4$ – K_2X – H_2O besides confirming the existence of the above compounds indicate the presence of yet another specie $(\text{ThX})^{++}$ in all these systems. Attempts at isolation of this last specie however, failed because of the ease with which it was decomposed into ThX_2 . The system $\text{Th}(\text{NO}_3)_4$ – $\text{K}_2\text{C}_2\text{O}_4$ – H_2O has also been studied for the sake of the completeness of the investigation.

Introduction

Although the oxalatocomplexes of thorium have been studied by a number of workers¹⁻³), malonato, succinato and adipato complexes of this element have not received the same amount of attention. Very little work has been done on the malonato complexes of thorium but surprisingly quite a good amount of literature has accumulated on the malonato complexes of a number of other elements⁴). BRINTZINGER and JOHN⁵) studied the malonato complexes of thorium by dialysis and showed the existence of the single shelled-anions. The complexes of

1) J. F. BOHR, *Annalen* **132**, 231 (1864).

2) R. W. BUNSEN, *Pogg. Annalen* **155**, 375 (1875).

3) B. BRAUNER, *J. chem. Soc.* **73**, 951 (1848).

4) P. T. CLEVE, *Bull. chem. Soc.* **21**, 116 (1874).

5) A. ROSENHEIM and Coworkers, *Z. anorg. allg. Chem.* **35**, 424 (1903).

6) C. JAMES, C. F. WHITTEMORE, and H. C. HOLDEN, *Amer. chem. Soc.* **36**, 1853 (1914).

7) R. J. MEYER and O. HAUSER, *Anal der Seltene Erden und Erd Sauren*.

8) H. T. S. BRITTON and MAURICE E. D. JARRET, *J. chem. Soc.* **1936**, 1494.

9) H. T. S. BRITTON and MAURICE E. D. JARRET, *J. chem. Soc.* **1935**, 1728.

10) H. BRINTZINGER and F. JOHN, *Z. anorg. allg. Chem.* **235**, 115 (1937).

thorium with some dicarboxylic acids have been investigated from measurements of conductivity and absorption of light by BOBTELSKY and BAR GODDA¹¹⁾.

KUAN PAN and CHENG¹²⁾ have very recently investigated these complexes by conductometric and electrometric titrations.

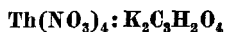
An examination of the literature shows that further work is desirable in which the preparative and physico-chemical investigations are combined to find the composition of the compounds formed in these systems. Hence in the present investigation the molanato, succinato and adipato complexes of thorium have been studied both from the preparative and physico-chemical view points. The oxalato complexes have also been studied for the sake of the completeness of the investigation.

Preparative Studies

For preparative work all the chemicals used were of B.D.H.(L.R) quality. Potassium malonate, oxalate, succinate and adipate used in these studies were prepared by titrating the dibasic acids with potassium hydroxide.

Solution of $\text{Th}(\text{NO}_3)_4$ and K_2X were taken in different molar ratios. In molar ratios where a precipitate was obtained either in the cold, immediately or on standing or on heating, it was filtered, washed and dried at 100—105 °C. But in molar ratios where a clear solution was obtained, the thorium compound formed by a metathetic reaction was isolated by fractional crystallization. The various compounds prepared either by precipitation or by fractional crystallization have been analyzed. Potassium has been estimated by LANGE flame photometer. Thorium in the insoluble compounds has been estimated as ThO_2 simply by igniting a known weight of such compounds. But in the crystalline compounds it has been estimated after the removal of the interfering acids by oxalate method. Malonate has been estimated by oxidizing it in hot dilute sulfuric acid medium with a known excess of ceric sulphate and back titrating the unreacted amount with ferrous ammonium sulfate, using O-phenanthroline as indicator.

The data of the analysis of the various compounds prepared as above from the various molar ratio of reactants is summarized below:

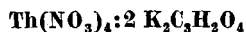


Found Th 49.40, malonate 43.35,

$\text{Th}(\text{C}_3\text{H}_2\text{O}_4)_2 \cdot 2 \cdot \text{HO}$ requires Th 49.27 and malonate 43.21%.

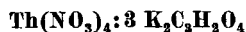
¹¹⁾ M. BOBTELSKY and I. BAR GODDA, Bull. chim. Soc. (France) **1953**, 276.

¹²⁾ KUAN PAU and H. S. CHENG, Natl. Taiwan Univ., J. Chin. chem. Soc. (Taiwan) **]]-3**, 1—12 (1956).



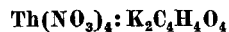
Found Th 49.15, malonate 43.0,

$\text{Th}(\text{C}_3\text{H}_2\text{O}_4) \cdot 2 \text{H}_2\text{O}$ requires Th 49.27 and malonate 43.21%.



Found Th 37.18, malonate 49.20, K 12.35,

$\text{K}_2\text{Th}(\text{C}_3\text{H}_2\text{O}_4)_3$ requires Th 37.66, malonate 49.64 and K 12.69%.



Found Th 49.98, $\text{Th}(\text{C}_4\text{H}_4\text{O}_4)_2$ requires Th 50.02%.



Found Th 44.24, $\text{Th}(\text{C}_6\text{H}_8\text{O}_4)_2$ requires Th 44.64%.

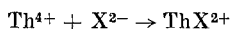
Physico-chemical Studies

For physico-chemical measurements all the chemicals used were of B.D.H.(A.R.) quality.

Heterometric Titrations

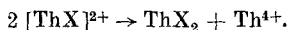
On adding slowly with constant stirring the potassium salts of the dicarboxylic acids from a burette to a given volume of thorium nitrate solution, the following observations were made.

In all the cases a white precipitate is obtained which goes on dissolving till the molar ratio 1:1 is reached. This suggests the formation of the complex ion $(\text{ThX})^{2+}$ (where X = oxalate, malonate, succinate or adipate).

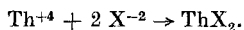


with oxalate the white precipitate obtained in the beginning appears to dissolve only partially in the excess of thorium nitrate solution. This indicates that $[\text{ThC}_2\text{O}_4]^{2+}$ is probably much more unstable than the corresponding malonato, succinato and adipato complex ions.

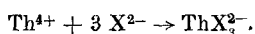
The complex ion $[\text{ThX}]^{2+}$ either on standing or on heating gets decomposed into ThX_2 as follows:



Addition of K_2X beyond the molar ratio 1:1 results in the formation of a white precipitate which does not dissolve but goes on thickening till the molar ratio is 1:2. The thick white precipitate as shown by analysis and by stoichiometry of the reaction is of ThX_2 .



Further additions of K_2X in the case of malonate and oxalate dissolves the precipitate and the dissolution process becoming complete when the molar ratio 1:3 has been reached. This indicates the formation of the complex ion $[\text{ThX}_3]^{2-}$ as follows:



As the precipitates of thorium succinate and adipate do not dissolve in excess of the potassium salts, the existence of the anionic complexes of thorium in these cases is ruled out.

Conductivity and p_H -Measurements

Conductivity and p_H -measurements were carried out as in our earlier communication dealing with zirconium compounds of some dicarboxylic acids¹³). The results of conductivity and p_H studies are represented graphically in curves 1–8.

From an examination of the curve (1) the existence of the following species is evident $\text{Th}(\text{C}_3\text{H}_2\text{O}_4)^{2+}$, $\text{Th}(\text{C}_3\text{H}_2\text{O}_4)_2$ and $[\text{Th}(\text{C}_3\text{H}_2\text{O}_4)_3]^{2-}$. The increase in conductivity from A to B in the above curve is due to the formation of an unstable complex ion, $[\text{Th}(\text{C}_3\text{H}_2\text{O}_4)]^{2+}$ which gets largely dissociated into its constituent ions. That this is so is confirmed by the formation of thorium malonate from a solution containing $\text{Th}(\text{NO}_3)_4$ and potassium malonate in the molar ratio of 1:1 either on standing or on heating. Decrease in conductivity from B to C may be due to the removal of thorium ions from solution on account of the formation of a sparingly soluble thorium malonate.

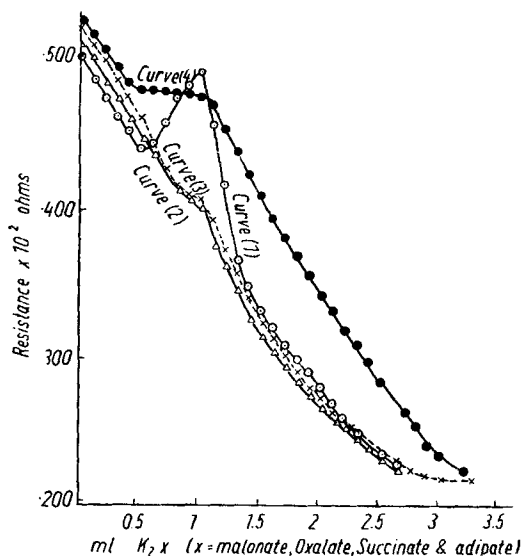


Fig. 1. Conductometric titrations of 10 ml. of M/20 $\text{Th}(\text{NO}_3)_4$ with M-Pot. Malonate (Curve 1), M-Pot. Oxalate (Curve 2), M-Pot. Succinate (Curve 3) and M-Pot. Adipate (Curve 4)

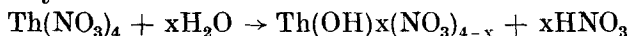
thorium malonate to form a complex ion, $[\text{Th}(\text{C}_3\text{H}_2\text{O}_4)]^{2-}$ possessing a high value of secondary dissociation. There is a regular increase of conductivity from D to E, which suggests that the higher complex anions such as $[\text{Th}(\text{C}_3\text{H}_2\text{O}_4)_4]^{4-}$ if at all formed, are exceedingly unstable.

In curves 2–4 the values of resistance have been plotted against the concentration of K_2X ($\text{X} = \text{oxalate, succinate and adipate}$). All these

¹³) R. C. AGGARWAL, S. P. AGRAWAL and T. N. SRIVASTAVA, Z. anorg. allg. Chem. (under publication).

curves exhibit an inflexion corresponding to the formation of the compound ThX_2 . The inflexion corresponding to $(\text{ThX})^{++}$ is, however, not very clear in these curves although an increase of conductance upto the molar ratio 2:1 (of Th^{+4} and X^{2-} ions) would suggest the existence of such a specie. The absence of an inflexion at the molar ratio 1:3 in the curves 3 and 4 is quite understandable as no anionic complexes of thorium have been found to exist in these systems either by the preparative methods or by heterometric titrations. In the case of oxalate (curve) where the anionic complex $[\text{Th}(\text{C}_2\text{O}_4)_3]^{2-}$ has been found to exist definitely the absence of the inflexion point may be explained due to the strong secondary dissociation of the complex which takes it into the category of a double salt.

Curves 5—8 represent the pH titrations of 20 c. c. $\text{M}/20$ $\text{Th}(\text{NO}_3)_4$ containing respectively 0, 1, 2 and 3 c. c. $\text{K}_2\text{C}_3\text{H}_2\text{O}_4$ (M) against molar KOH. The small but regular increase of pH from A to B and then from B to C in curve 5 may be due to the neutralization of the nitric acid present in thorium nitrate solution due to hydrolysis.



since a total of three equivalents of potassium hydroxide is required for the neutralization of the above acid, it appears that what is precipitated is a basic nitrate of thorium and not pure thorium hydroxide. The value of x appears to be 3. Further additions of potassium hydroxide beyond C results in a rapid increase of pH due to the accumulation of free alkali. Initially higher values of pH in curves 6—8 are probably due to the reac-

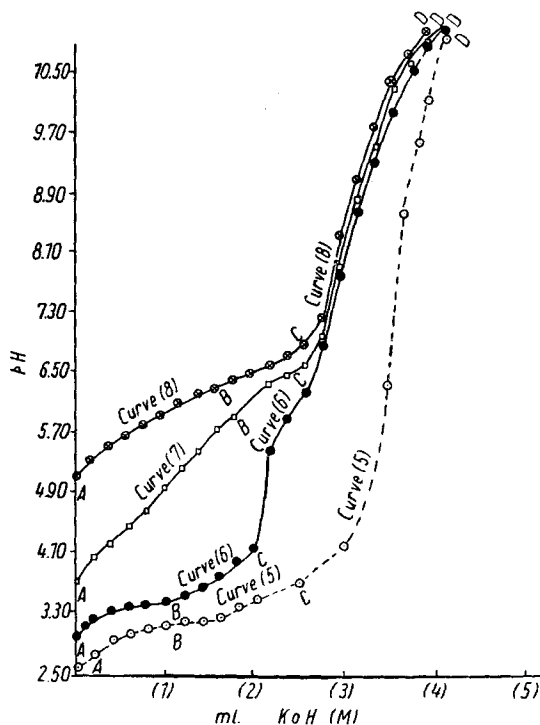


Fig. 2. Potentiometric titrations of 20 ml. of $\text{M}/20$ $\text{Th}(\text{NO}_3)_4$ with molar KOH solution (Curve 5) and in the presence of 1 (Curve 6), 2 (Curve 7) and 3 (Curve 8) moles respectively of Potassium malonate per mole of thorium nitrate

tion between nitric acid (present in thorium nitrate solution due to hydrolysis) with potassium malonate to produce malonic acid, a weak acid. Nature of the curve 6 is similar to that of the curve 5 with the only difference that the portion BC in it is nearly halved. This is due to conversion of half of the thorium ions by potassium malonate into the sparingly soluble thorium malonate through the decomposition of the unstable complex ion $(\text{ThC}_3\text{H}_4\text{O}_4)^{2+}$.

The portion BC in curve 7 nearly disappears showing that the whole of thorium is present in the form of the sparingly soluble thorium malonate before the titration with potassium hydroxide is started. This shows that unlike in curves 5 and 6, the potassium-hydroxide in curve 7 is used merely for the neutralization of the acid present in the solution (before the titration is commenced) and none for the precipitation of basic thorium nitrate.

The appearance of the portion BC again in curve 8 in which the molar ratio of Th^{4+} and $\text{C}_3\text{H}_2\text{O}_4^{2-}$ ion is 1:3, shows that some of the potassium

hydroxide is used for changing thorium ions, resulting from the secondary dissociation of the unstable complex $[\text{Th}(\text{C}_3\text{H}_2\text{O}_4)_3]^{2-}$ into the basic salt.

In curve 9, there are as before three characteristic portions viz. AB, BC and CD.

The slight increase of p_{H} from A to B is due to the replacement of strong nitric acid in thorium nitrate

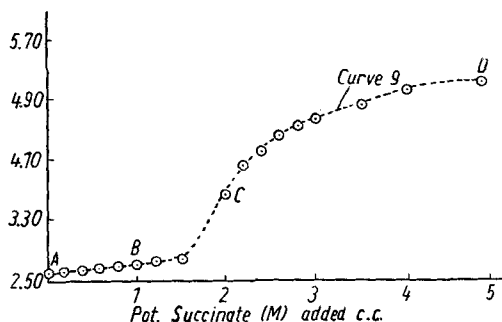


Fig. 3. Potentiometric titration of 20 c.c. of M/20 $\text{Th}(\text{NO}_3)_4$ with molar Pot. Succinate

solution (on addition of potassium succinate) by weak succinic acid. From B to C two equivalents of potassium succinate are used evidently for the formation of thorium succinate. From C to D there is only slight increase of p_{H} showing that the ionizable complex $[\text{Th}(\text{C}_4\text{H}_4\text{O}_4)_3]^{2-}$ is not formed in this system.

The fact that although $[\text{Th}(\text{C}_2\text{O}_4)_3]^{2-}$ and $[\text{Th}(\text{C}_3\text{H}_2\text{O}_4)_3]^{2-}$ have been found to exist, the corresponding succinato and adipato compounds have been found to be non-existent, finds ready explanation when it is recollected that while oxalato and malonato complexes involve, five and six membered rings, the succinato complexes would therefore involve 7 membered rings which are rare and adipato complexes would involve still higher membered rings which are practically unknown.

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