Electrometric Studies on Thorium Arsenates as a Function of pH

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The formation and composition of thorium arsenates obtained by the interaction of thorium nitrate and different alkali arsenates (meta, pyro and ortho) at specific pH levels 7.2, 8.3 and 11.1 have been studied by employing electrometric techniques involving amperometric, pH, potentiometric and conductometric titrations. The results provide cogent evidence for the formation of three thorium arsenates having the molecular formulae ThO₂·2As₂O₅, ThO₂·As₂O₅ and 3 ThO₂·2As₂O₅ in the vicinity of pH 4.2, 4.9 and 5.6 respectively. Analytical investigations of the compounds have also been carried out which substantiate the results of electrometric study.

A survey of literature reveals that there are meagre references on the study of thorium arsenates. BARBERI ¹ treated aq. arsenic acid (40%) with boiling solution of thorium nitrate (2% thoria) to get thorium mono hydrogen ortho arsenate Th(H₂AsO₄)₂·6H₂O as a crystalline precipitate; whereas he obtained thorium-di-hydrogen orthoarsenate, Th(H₂AsO₄)₁·4H₂O, by using 50% of aq. arsenic acid and thorium nitrate solution containing 5% thorium. He further reported that more dilute solutions of reagents give gelatinous precipitates of variable composition. PIERRE CASTEL ² obtained crystals of Th(H₂AsO₄)₁·6H₂O and Th(H₂AsO₄)₂·5H₂O by mixing ThO₂·As₂O₅ in the ratios 0.05 to 0.14 and 1.63 to 5.80, respectively. GILLES LE FLEM, JACQUES LAMIC and PAUL HAGENMULLER ³ prepared two allotropic form of Th(As₂O₄)₄ by temperature treatment of mixtures of As₂O₅ — ThO₂ gel and arsenic acid. They observed that the products of heating the gel strongly were two form s of the pyro arsenate Th₃As₄O₁₁ and the hexa arsenate Th₄As₆O₂₃ and the ortho arsenate Th₃(AsO₄)₄.

In view of the insufficient and conflicting reports of earlier workers on the composition of thorium arsenates, and in the absence of any electrometric data on the subject, it was considered worthwhile to study the formation and composition of thorium arsenates obtained by the interaction of thorium nitrate and alkali arsenates at different pH levels, by means of electro-metric techniques which have provided more conclusive evidences on the composition of such and allied compounds ⁴-¹³.

Experimental

Merk’s guaranteed extra pure reagents, As₂O₅, Th(NO₃)₄, NaOH and Quinhydrone were used. Air-free conductivity water was used in the preparation of solutions. As₂O₅ solution was further estimated as silver arsenate ¹⁴ and thorium as ThO₂ via its oxalate ¹⁴. Solutions of different arsenates were prepared by adding calculated amounts of NaOH to boiling solution of As₂O₅ of the required strength. A manual polarograph with scalamp galvanometer as current recorder was employed for performing amperometric titrations. A capillary having the following characteristics, m = 2.416 mg/Sec, t = 3.58 sec, and m²t⁻¹/³ = 2.226 mg² sec⁻¹/³ was used in conjuction with a saturated calomel electrode connected to the cell by a low resistance salt bridge. Twenty ml. of titre solution was taken in the cell each time and hydrogen gas was used for deaeration and stirring of solutions. Amperometric titrations were carried out at a potential

² PIERRE CASTEL, C. R. hebld. Séances Acad. Sci. 206, 37 [1939].
³ GILLES LE FLEM, JACQUES LAMIC, and PAUL HAGENMULLER. Bull. Soc. chim. France 6, 188 [1966].
⁵ R. S. SAXENA and M. L. MITTAL, J. inorg. nuclear Chem. 27, 2553 [1965].
⁸ R. S. SAXENA and C. S. BHATNAGAR, J. inorg. nuclear Chem. 12, 38 [1959].
of $-1.6$ volts (vs. S.C.E.) using 0.001% Triton X-100 as a maximum suppressor. The pH and e.m.f. values were measured on a Cambridge null deflection type pH meter, using a wide range glass electrode and a quinhydrone indicator electrode respectively, in conjunction with S.C.E. Conductance measurements were performed on LBR type conductometer (W Germany). 25 ml of titre solution was taken in the cell each time.

Using different concentrations of the reactants, a series of amperometric pH, e.m.f. and conductometric titrations were performed in aqueous and aqueous alcoholic media. Four representative graphs illustrating amperometric (fig. 1), pH (fig. 2), e.m.f. (fig. 3), and conductometric (fig. 4) titrations of meta, pyro, and ortho arsenates have been given and the electrometric results summarised in tables I and II.

**Discussion**

The different arsenates were prepared by progressive additions of NaOH solution to boiling solution of As$_2$O$_5$ in the molecular ratio 2:1, 4:1 and 6:1, the corresponding compounds formed were:

$$2 \text{NaOH} + \text{As}_2\text{O}_5 = 2 \text{NaAs}_2\text{O}_4 + \text{H}_2\text{O}.$$ $$4 \text{NaOH} + \text{As}_2\text{O}_5 = \text{Na}_4\text{As}_2\text{O}_7 + 2 \text{H}_2\text{O}.$$ $$6 \text{NaOH} + \text{As}_2\text{O}_5 = 2 \text{Na}_3\text{As}_4\text{O}_{10} + 3 \text{H}_2\text{O}.$$
and their pH was found to be 7.2, 8.3 and 11.1 respectively.

**Sodium meta-arsenate titrations:** Fig. 2 (curves 1 and 4) illustrates the changes occurring in H⁺ concentration when thorium nitrate solution (pH 3.6) is treated with NaAsO₃ solution (pH 7.2). In direct titrations, curve 1, when Th(NO₃)₄ solution was added from the microburette to NaAsO₃ solution, a gradual change in pH was observed till at the stoichiometric end point (the stage at which the reaction ends if simple double decomposition takes place), a sharp fall in pH was noted with the inflection corresponding to the molar ratio of ThO₂: As₂O₅ as 1:2, suggesting the formation of thorium meta-arsenate ThO₂·2 As₂O₅ in the vicinity of pH 4.2. In the case of reverse titrations, (curve 4), when NaAsO₃ solution was used as the titrant, the pH first increases slowly but at the stoichiometric end point a marked jump in pH was observed, suggesting the formation of the same compound according to the equation

\[
\text{Th(NO}_3)_4 + 4 \text{NaAsO}_3 \rightarrow \text{ThO}_2 \cdot 2 \text{As}_2\text{O}_5 + 4 \text{NaNO}_3.
\]
Molarity of solutions | Calc. | Equivalence points [ml] observed from pH | Molarity of solutions | Calc. | Equivalence points [ml] observed in presence of 0% alc. | Pyro-arsenate titrations | Direct titrations. Fig. 1, Curve 1
---|---|---|---|---|---|---|---
Th(NO₃)₄ Na₄As₂O₇ | [M/₈] | Meta-arsenate titrations | Direct titrations. Figs. 3, 4 and 4. Curve 1
| 30 | 80 | 2.34 | 2.35 | 2.35 | 2.3 | 100 | 800 | 2.57 | 2.6 | 2.65 | 2.55 | 2.5
| 50 | 100 | 3.12 | 3.0 | 3.0 | 2.95 | 150 | 1000 | 3.0 | 3.0 | 3.0 | 2.5 | 2.5
| 80 | 200 | 2.50 | 2.4 | 2.45 | 2.45 | 2.8 | 1000 | 140 | 2.85 | 2.85
| 20 | 100 | 3.33 | 3.35 | 3.35 | 3.4 | 600 | 350 | 3.33 | 3.35 | 3.35 | 2.85 | 2.85
| 400 | 20 | 2.50 | 2.55 | 2.55 | 2.6 | 400 | 40 | 2.66 | 2.7 | 2.55 | 2.55
| 750 | 20 | 2.66 | 2.7 | 2.8 | 2.75 | 750 | 40 | 2.7 | 2.75 | 2.75 | 2.55
| 900 | 30 | 3.33 | 3.35 | 3.45 | 3.4 | 900 | 50 | 3.22 | 3.22 | 3.22 | 2.75

Ortho-arsenate titrations

| Th(NO₃)₄ Na₃AsO₄ | Direct titrations. Figs. 3, 4 and 4. Curve 6
| 20 | 10 | 2.66 | 2.65 | 2.65 | 2.65 | 2.65 | 600 | 50 | 2.7 | 2.7 | 2.75 | 2.75
| 350 | 30 | 2.85 | 2.85 | 2.85 | 2.85 | 2.85 | 750 | 40 | 2.85 | 2.85 | 2.85 | 2.85
| 450 | 40 | 2.96 | 3.0 | 3.0 | 3.0 | 3.0 | 900 | 50 | 3.22 | 3.22 | 3.22 | 3.22

Table II. Summary of the results of amperometric titrations.  
Titrations were performed at $E_{d,e} = -1.6$ V (vs. S.C.B.) at which Th⁺⁺⁺ yields a well defined reduction wave while arsenates ions do not produce any diffusion current. The titration curves provide well defined breaks at a point (see table II), where the molecular ratio of ThO₂ and As₂O₅ is as 1:1, suggesting the precipitation of thorium pyro-arsenate, ThO₂·As₂O₅, in the neighbourhood of pH 4.9. The reaction can be represented as follows:

$$\text{Na}_4\text{As}_2\text{O}_7 + \text{Th(NO}_3)_4 = \text{ThO}_2\cdot\text{As}_2\text{O}_5 + 4\text{NaNO}_3.$$  

Several direct and reverse pH (fig. 2, curves 2 and 5), e.m.f. (fig. 3, curves 2 and 5), and conductometric (fig. 4, curves 2 and 5) titrations of sodium pyro-arsenate were carried out with thorium nitrate solution. The end points obtained from the curves (see table I) indicated the reacting ratio of ThO₂:As₂O₅ as 1:1, confirming the formation of thorium pyro-arsenate.

Sodium ortho-arsenate titrations: Amperometric (fig. 1, curves 2 and 4), pH (fig. 2, curves 3 and 6), and conductometric (fig. 4, curves 3 and 6) titrations performed between thorium nitrate (pH 3.6) and sodium ortho-arsenate (pH 11.1) solution yield well defined inflections and breaks at a point where the molar ratio of ThO₂:As₂O₅ is as 3:2 corresponding to the formation of thorium ortho-arsenate, 3ThO₂·2As₂O₅ at pH 5.6 according to the reac-

Table I. Summary of the results of pH, e.m.f. and conductometric titrations.

Employing similar concentrations of the reactants, potentiometric (fig. 3, curves 1 and 4), and conductometric, (fig. 4, curves 1 and 4) titrations were carried out. Well defined inflections and breaks are obtained at the stoichiometric end points corresponding to the molar ratio of ThO₂:As₂O₅ as 1:2 and confirm the formation of the identical compound, thorium meta-arsenate ThO₂·2As₂O₅. Amperometric titrations were also tried but they were found unsuccessful.

Sodium pyro-arsenate titrations: Sodium pyro-arsenate solution (pH 8.3) was prepared as described earlier and a series of direct, (fig. 1, curve 1), and reverse, (fig. 1, curve 3), amperometric titra-

Table II. Summary of the results of amperometric titrations.
tion:

$$3 \text{Th}(\text{NO}_3)_4 + 4 \text{Na}_3\text{AsO}_4 = 3\text{ThO}_2 \cdot 2\text{As}_2\text{O}_5 + 12\text{NaN}_3$$

It is noted that after each addition of the titrant it took a little time for the pH, e.m.f., and conductance values to become steady. A thorough stirring in the neighbourhood of the equivalence point has a favourable effect. Each titration takes about half an hour for completion. The presence of ethyl alcohol slightly improves the position of the end points and increases the magnitude of the jump in pH and e.m.f., as it decreases the solubility of the precipitates formed and minimises hydrolysis and adsorption.

**Analytical study:** Analytical investigations were also carried out with a view to substantiate the electrometric results. Thorium meta-, pyro-, and ortho-arsenates were prepared by mixing the stoichiometric amounts of thorium nitrate and respective arsenates. The precipitate obtained in each case was washed several times with 10% ethanolic water and dried completely by keeping it in an oven at 110 °C for 6 hours and then in vacuum desiccator for 24 hours. A known amount of each (2 gms.) was dissolved in minimum quantity of dilute HCl and then analysed quantitatively for thorium and arsenic. Thorium was estimated as its oxide via thorium oxalate and arsenic iodometrically. From the proportions of ThO₂ and As₂O₅ in the compounds thus obtained, their compositions were established, which were found to be the same as obtained by electrometric methods.

The above electrometric and analytical studies confirm the formation of three thorium arsenates, viz. ThO₂·2As₂O₅, ThO₂·As₃O₅ and 3ThO₂·2As₂O₅ in the vicinity of pH 4.2, 4.9 and 5.6 respectively.

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Über Phosphazene, XXX

**Zur Ammonolyse von Chlorphosphorananen**

The ammonolysis of phosphorus(V) chlorides

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The ammonolysis of a chlorophosphorane is characterised by the side by side substitution and condensation competing with one another. The different results fit into one reaction model from which the determining factors may be derived. Within the normal temperature range condensation proceeds only as long as both Cl and NH₂ functions at the phosphorus are present.

Presubstitution by dialkylamines reduces condensation. Thus the partially alkylsubstituted tetraamino phosphonium and hexaamino diphosphorus nitride salts $P(NR₂)₂(NH₂)₂^+$, $N[P(NR₂)(NH₂)]₂^+$ and $N[P(NR₂)₂(NH₂)]₂^+$ are synthesised.

**Die Ammonolyse von Phosphorpentachlorid**

Sie darf als die klassische Reaktion der Phosphazenechimie gelten. Ihr schenkte schon 1811 DAVY seine Aufmerksamkeit und ihre detaillierte Klärung beansprucht auch noch das Interesse unserer Tage. Ohne besondere Vorkehrungen durchgeführt, liefert die Umsetzung von $\text{PCl}_5$ mit NH₃ ein weißes Reaktionsprodukt, das sich mit Wasser auftrennen läßt. LIEBIG schreibt 1832 dazu an WÖHLER: „Das Wasser enthielt nur Salmiak und keine Spur von Phosphorsäure; der Phosphor muß also in die Zusammensetzung des weißen Körpers eingegangen sein.“

Dieser Körper hat die idealisierte Zusammensetzung $\text{PN}_5\text{H}^5$—7, entsteht nach

$$\text{PCl}_5 + 7 \text{NH}_3 \rightarrow 5 \text{NH}_4\text{Cl} + \text{PN}_5\text{H}$$

4 J. LIEBIG u. F. WÖHLER, Liebigs Ann. Chem. 11, 139 (1834).

