

The Preparation of Thorium Alkoxides.

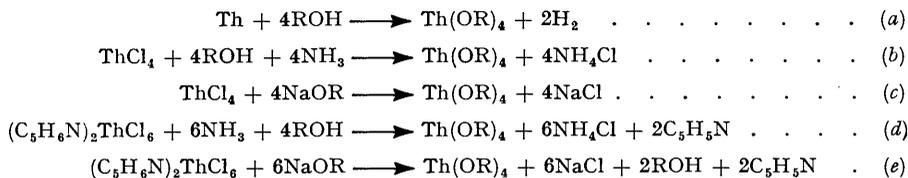
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By means of reactions involving thorium tetrachloride alcoholates $\text{ThCl}_4 \cdot 4\text{ROH}$ or pyridinium thorium hexachloride $(\text{C}_5\text{H}_5)_2\text{ThCl}_6$ with ammonia or sodium alkoxides, thorium tetra-alkoxides $\text{Th}(\text{OR})_4$ ($\text{R} = \text{Me}$, Et or Pr^i) have been prepared. They are complex, non-volatile, and alkaline. These properties are discussed from the theoretical standpoint.

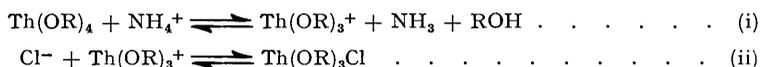
RECENT work on the structural chemistry of the alkoxides of Group IVA elements (Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 4204) suggested that thorium alkoxides should possess some interesting properties. These appear not to have been prepared hitherto.

Experience with titanium, zirconium, and hafnium suggested the following possible methods for preparing thorium alkoxides :



It was not possible to realise method (a) although several substances, *e.g.*, HgCl_2 , I_2 , $\text{Zr}(\text{OEt})_4 \cdot \text{CH}_3 \cdot \text{COCl}$, etc., were tried as catalysts. This failure of thorium to react is interesting in comparison with the behaviour of other metallic elements with alcohols. Thus it is well-known that the alkali metals, magnesium, and aluminium react vigorously with the lower alcohols although for magnesium and aluminium catalysts are required.

The other methods met with various degrees of success. When ammonia was used [methods (b) and (d)] the resulting thorium compounds contained appreciable percentages of chloride whereas the products from methods (c) and (e) were chloride-free. This behaviour was readily understood when it was found that alcoholic solutions of thorium ethoxide or thorium *isopropoxide* were alkaline to thymolphthalein. On the other hand anhydrous ammoniacal alcohol was acidic to this indicator. Thus thorium alkoxides are more basic than ammonia and the following equilibria are feasible :



Ammonium chloride is appreciably soluble in ammoniacal alcohol and thus affords the ions required to favour the products on the right-hand sides of (i) and (ii). There is little doubt that the complete replacement of chloride effected by sodium alkoxides is caused by the low solubility of sodium chloride in alcohols.

The best results were obtained with method (c) involving the reaction between $\text{ThCl}_4 \cdot 4\text{Pr}^i\text{OH}$ and sodium *isopropoxide*. Thorium tetra*isopropoxide* was a white solid, very soluble in *isopropyl* alcohol or benzene, and sublimed at $200\text{--}210^\circ/0.05\text{--}0.1$ mm. It was instantly hydrolysed, even by traces of water. Ebullioscopic measurements in benzene and in *isopropyl* alcohol gave molecular complexities of 3.8 and 1.8 respectively. The high complexity in benzene was not surprising in view of the low volatility of thorium *isopropoxide*. Moreover, zirconium *isopropoxide* (b. p. $160^\circ/0.1$ mm.) is trimeric in benzene and stereochemical considerations would predict a lower volatility and higher complexity for thorium *isopropoxide*. The lower complexity in *isopropyl* alcohol can be attributed to the "donor" nature of the solvent and the greater ionic dissociation of thorium *isopropoxide* in this solvent. The latter possibility is being investigated conductometrically.

Preliminary experiments on the preparation of thorium ethoxide by the methods (b), (d), and (e) gave a benzene-soluble product which was not the pure ethoxide. It contained

chlorine and products of hydrolysis. Later work employing improved means of avoiding hydrolysis showed that pure thorium ethoxide was only sparingly soluble in benzene or ethyl alcohol. In one experiment most of the thorium ethoxide was co-precipitated with sodium chloride and was less hydrolysed than the thorium ethoxide remaining in solution. Consequently these methods are unsuitable for preparing thorium ethoxide, and the pure compound was obtained from the *isopropoxide* by alcohol interchange: $\text{Th}(\text{OPr}^i)_4 + 4\text{EtOH} \longrightarrow \text{Th}(\text{OEt})_4 + 4\text{Pr}^i\text{OH}$.

The ethoxide was so sparingly soluble in benzene or ethyl alcohol as to preclude the determination of its molecular weight. It is interesting that the solubility of zirconium ethoxide in benzene is also very sensitive to impurity, and in the same sense. The pure zirconium compound is transformed by fusion into a soluble form which reverts to the insoluble form after crystallisation from benzene; but pure thorium tetraethoxide has no melting point and no soluble form was obtained.

Thorium tetramethoxide, a white insoluble powder [like $\text{Zr}(\text{OMe})_4$], was prepared from the *isopropoxide* by alcohol interchange. Neither the tetramethoxide nor the tetraethoxide of thorium could be sublimed below 300° at 0.05 mm. and above this temperature pyrolysis occurred.

Unlike titanium and zirconium, thorium derivatives do not form complex lower alkoxides with sodium alkoxides. Moreover, the stability of the sodium zirconium alkoxides appears to be much greater than that for the titanium derivatives, as judged by the behaviour of the metal tetrachlorides with sodium alkoxides: titanium tetraalkoxides are thus obtained, yet the addition of exactly four equivalents of sodium ethoxide to one mole of zirconium tetrachloride gives no zirconium tetraethoxide but, instead, a complex sodium zirconium ethoxide. The behaviour of thorium tetrachloride with sodium alkoxide resembles that of titanium tetrachloride. For example, thorium *isopropoxide* is readily obtained by the reaction: $\text{ThCl}_4 + 4\text{NaOPr}^i \longrightarrow \text{Th}(\text{OPr}^i)_4 + 4\text{NaCl}$. Addition of sodium *isopropoxide* (1 equiv.) to thorium *isopropoxide* (1 mol.) gave no crystalline sodium-thorium complex, and thorium *isopropoxide* was recovered by sublimation under reduced pressure. The tendency of the lower alkoxides of titanium, zirconium, and thorium to combine with sodium alkoxides appears to be in the order $\text{Ti} \ll \text{Zr} \gg \text{Th}$. The different behaviour of titanium and zirconium alkoxides may be due to a combination of steric and electronic effects, but the contrast between the derivatives of zirconium and thorium is presumably a result of electronic factors alone. Thus zirconium appears to be comparatively electrophilic because zirconium alkoxides are acidic towards thymolphthalein and can be titrated to a sharp end-point with sodium alkoxides. However, although thorium alkoxides are complex substances and probably involve thorium in either 6 or 8 co-ordination with oxygen, it is clear that the electropositive nature of the thorium atom predominates because the alkoxides are definitely alkaline towards thymolphthalein and do not appear to form compounds with sodium alkoxides.

EXPERIMENTAL

Apparatus.—All-glass apparatus of the type previously described (*loc. cit.*) was used. For the addition of sodium *isopropoxide*, which is sparingly soluble in *isopropyl alcohol*, to the thorium halides a Soxhlet apparatus proved most satisfactory. Exceptional precautions were necessary to avoid hydrolysis of the new compounds, for once hydrolysis had occurred none of the substances described below could be purified by crystallisation or sublimation. Air or nitrogen admitted to an apparatus was dried first with silica gel and finally with phosphoric oxide. "Portex" tubing was used in place of rubber tubing for the connection of the phosphoric oxide tube to the apparatus.

Materials.—The preparation of pyridinium thorium hexachloride and the alcoholates of thorium chloride will be described in another communication.

Very dry ethyl alcohol (water content *ca.* 0.003%) was prepared from "absolute" alcohol by first drying it azeotropically with benzene and then adding sodium ethoxide and diethyl phthalate.

"AnalaR" *isopropyl alcohol* was dried (to water content *ca.* 0.007%) by the azeotropic method in a fractionating column (120 cm.) packed with Fenske glass helices.

Methyl alcohol was dried by refluxing it with freshly prepared magnesium methoxide.

Ammonia gas from a cylinder was dried over freshly ignited quicklime.

Analytical Methods.—Thorium was determined by precipitating thorium hydroxide and igniting this to the dioxide. The alkoxide radicals were determined by the volumetric method previously described (*loc. cit.*).

Preparation of Thorium Ethoxide.—(1) *From thorium tetrachloride tetraethyl alcoholate.* A solution of the alcoholate $\text{ThCl}_4 \cdot 4\text{EtOH}$ (20.35 g.) in ethyl alcohol (33 g.) and benzene (45 g.) was treated with excess of ammonia. After completion of the exothermic reaction the free ammonia was removed under reduced pressure and the ammonium chloride by filtration. The filtrate was evaporated to dryness under reduced pressure and gave impure thorium tetraethoxide as a white solid (12.75 g.) [Found: Th, 57.6; OEt, 40.8; Cl, 1.6. Calc. for $\text{Th}(\text{OEt})_4$: Th, 56.3; OEt, 43.7%].

(2) *From pyridinium thorium hexachloride.* The complex thorium chloride $(\text{C}_5\text{H}_5\text{N})_2\text{ThCl}_6$ (15.9 g.) was suspended in ethyl alcohol (72 g.) and benzene (50 g.) and treated with excess of ammonia. After filtration, evaporation of the filtrate gave a white solid (8.37 g.) with a high chloride content (Found: Th, 58.2; OEt, 32.3; Cl, 8.3%).

In another experiment involving the complex thorium chloride (6.42 g.), ethyl alcohol (34 g.), benzene (45.5 g.), and excess of ammonia the filtrate obtained after the removal of ammonium chloride was evaporated to half-bulk and re-treated with ammonia. The final filtrate gave on evaporation to dryness a white solid (3.3 g.) with a lower chloride content (Found: Th, 56.6; OEt, 39.5; Cl, 2.5%).

In an attempt to obtain chloride-free thorium ethoxide the product (6.97 g.) containing 8.3% of Cl was dissolved in ethyl alcohol (70 g.) and treated with sufficient sodium ethoxide [from sodium (0.38 g.) in the Soxhlet apparatus] to combine with all the chloride. After filtration, a small quantity (1.4 g.) of solid was obtained by evaporation of the filtrate (Found: Th, 57.4; OEt, 38.1; Cl, 0.9%). The precipitate was a mixture of sodium chloride and thorium ethoxide, the latter being less hydrolysed ($\text{EtO} : \text{Th} = 3.98 : 1$) than the material ($\text{EtO} : \text{Th} = 3.43 : 1$) obtained from the filtrate.

(3) *From thorium tetraisopropoxide.* Thorium tetraisopropoxide (5.03 g.) was treated with boiling ethyl alcohol (160 g.) for 4 hr. A solid (2.8 g.) was obtained by filtration (Found: Th, 56.7; OEt, 42.6%). This was initially soluble in benzene but after one day had become insoluble in benzene or ethyl alcohol. The suspension in ethyl alcohol was alkaline to thymolphthalein.

Preparation of Thorium isoPropoxide.—(1) *Methods involving the use of ammonia.* (a) The alcoholate $\text{ThCl}_4 \cdot 4\text{Pr}^i\text{OH}$ (18.5 g.), suspended in isopropyl alcohol (43 g.) and benzene (200 g.), was treated with excess of ammonia. When reaction had ceased, free ammonia was removed under reduced pressure and the ammonium chloride filtered off. The filtrate was evaporated and left a highly viscous solid (12.23 g.) which was dried at 80° under reduced pressure [Found: Th, 51.3; OPr^i , 47.6; Cl, 2.2. Calc. for $\text{Th}(\text{OPr}^i)_4$: Th, 49.5; OPr^i , 50.5%].

At 0.1 mm. this product (0.67 g.) softened at 80° and sublimed at $200\text{--}210^\circ$. A white crystalline sublimate (0.29 g.) was obtained (Found: Th, 50.4; OPr^i , 49.0; Cl, 0.7%). Further sublimation did not improve the purity.

(b) The complex chloride $(\text{C}_5\text{H}_5\text{N})_2\text{ThCl}_6$ (12 g.), suspended in isopropyl alcohol (71 g.) and benzene (52 g.), was treated with excess of ammonia. After the removal of ammonium chloride by filtration the filtrate was evaporated to dryness under reduced pressure and gave a white solid (5.8 g.) (Found: Th, 52.8; OPr^i , 38.9; Cl, 7.0%). An attempt was made to lower the chloride content of this product by treatment with sodium isopropoxide. The foregoing product (4.9 g.) in boiling isopropyl alcohol (80 g.) was allowed to react with sodium isopropoxide produced from sodium (0.23 g.) in the Soxhlet extractor. The finely divided precipitate was removed by filtration through a sintered glass (No. 4) filter supporting a pad of "Hyflo-Supercel." The filtrate was evaporated to dryness under reduced pressure and gave a white solid (3.2 g.) (Found: Th, 50.7; OPr^i , 47.9; Cl, 0%).

(2) *Methods involving sodium isopropoxide.* (a) The complex pyridinium chloride (7.19 g.), suspended in isopropyl alcohol (60 g.), was heated in the boiler of a Soxhlet extractor, while sodium (1.62 g.) was in a sintered glass bucket in the extraction compartment. After about $\frac{1}{2}$ hr. the solutions in the boiler and in the extraction chamber had become yellow, probably owing to reaction between pyridine and metallic sodium. The brown solid (4.9 g.) obtained after the removal of sodium chloride and evaporation of solvent was chloride-free (Found: Th, 51.2%).

(b) The method from thorium tetrachloride tetraisopropyl alcoholate was most satisfactory for the preparation of pure thorium tetraisopropoxide and many experiments were conducted

with a view to finding the optimum conditions. The following exemplifies the final method. The alcoholate (35.9 g.) in isopropyl alcohol (280 g.) was caused to react with the sodium isopropoxide produced by combination of sodium (5.36 g.) in a Soxhlet apparatus (as above) with the boiling alcohol. A white solid (24.4 g., 89%) remained after the removal of sodium chloride and solvent in the usual way (Found: Th, 49.6; OPrⁱ, 50.2%). Thorium tetraisopropoxide appeared to melt at 110° under reduced pressure and a white crystalline sublimate was obtained at 200°/0.05 mm. The compound readily dissolved in isopropyl alcohol or benzene and in the former solvent it was alkaline to phenolphthalein and to thymolphthalein.

Molecular weights were determined ebullioscopically in both solvents, with the apparatus and methods previously described (*loc. cit.*) [Found: *M*, in benzene, 1760, in isopropyl alcohol, 861. Th(OPrⁱ)₄ requires *M*, 468]. The results were independent of concentration up to *ca.* 30 g./l. in benzene and *ca.* 25 g./l. in isopropyl alcohol.

Preparation of Thorium Tetramethoxide.—Thorium tetraisopropoxide (5.8 g.) was dissolved in benzene (50 g.). Methyl alcohol (130 g.) was added, a white gelatinous solid being precipitated. The mixture was boiled for 1 hr. and then evaporated to dryness. Analysis of the solid product (4.6 g.) (Found: Th, 65.0; OMe, 29.4%) suggested that interchange was not complete. The product was treated with more methyl alcohol (150 g.), and a white powder remained after evaporation to dryness [Found: Th, 66.6; OMe, 31.6. Calc. for Th(OMe)₄: Th, 65.2; OMe, 34.8%]. A sample of the methoxide was heated at 320°/0.05 mm. for 2 hr.; no sublimation occurred although the residue had decomposed (Found: Th, 71.4; OMe, 25.7%).

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