Alcoholates of Thorium Tetrachloride.

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The reactions of thorium tetrachloride with methyl, ethyl, *iso*propyl, *n*-butyl, and *tert.*-amyl alcohol and ethylene glycol have been studied. The results are discussed in terms of the theories previously advanced to account for the reactions of other Group IVA chlorides with alcohols.

It is well established that thorium tetrachloride reacts with ethyl alcohol to give $ThCl_4,4EtOH$, in marked contrast to the behaviour of the other Group IVA tetrachlorides. So far, the behaviour of other alcohols with thorium chloride has not been studied, and it appeared that such an investigation would yield results of special significance.

With methyl, ethyl, or *iso*propyl alcohols the products conformed to the general composition $ThCl_4,4ROH$ in which thorium shows a covalency of 8; the alcoholates should therefore behave as monomeric substances in solution. The molecular weight of the tetra(*iso*propyl alcoholate) was determined in boiling *iso*propyl alcohol; the apparent molecular complexity was less than unity. This result can best be explained in terms of an ionisation equilibrium, which suggestion received support from preliminary experiments that indicated a small but significant electrical conductance of $ThCl_4,4Pr^iOH$ in *iso*propyl alcohol. This behaviour is being further investigated.

In view of the apparent 8-co-ordination of thorium in these alcoholates we examined the behaviour of the dihydric alcohol, ethylene glycol. If the glycol molecule behaved as a " chelating " agent a substance with the formula $ThCl_4,2[C_2H_4(OH)_2]$ would be expected. When the *iso*propyl alcoholate was treated with an excess of ethylene glycol in boiling benzene, reaction was not confined to the alcohol interchange since some replacement of chlorine also occurred and the product had the ratio $Cl : Th = 3{\cdot}38$. Although this substance could not be purified, analysis demonstrated that it was not the simple derivative $ThCl_4,2[C_2H_4(OH)_2]$.

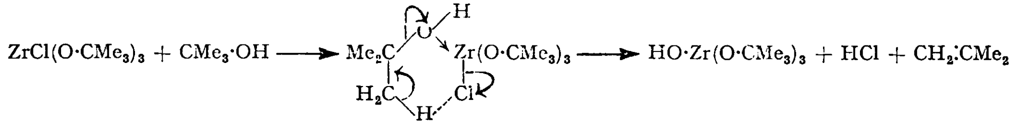
Anhydrous thorium chloride is much more difficult to prepare than the hydrated compound and we tried to use the latter as a starting material for the preparation of the alcoholates. Hecht (*Z. anorg. Chem.*, 1947, **254**, 37) has shown that certain metal chloride hydrates can be dehydrated with thionyl chloride or carbonyl chloride. We found that thionyl chloride effectively dehydrated hydrated thorium chloride and provided a product which, although not pure, was anhydrous: $ThCl_4,nH_2O + nSOCl_2 \longrightarrow ThCl_4 + nSO_2 + 2nHCl$. The impurity appeared to be a little thionyl chloride, which was retained even at 120°/0·1 mm. However, this anhydrous tetrachloride was successfully used to prepare the alcoholates since the occluded thionyl chloride reacted readily with the alcohol to give volatile products. The possibility of preparing the alcoholates directly from the hydrated tetrachloride was also explored and both ethyl and *iso*propyl alcoholates were prepared by azeotropic dehydration, benzene being used with the appropriate alcohol.

An interesting feature of the tetrachlorides of Group IVA elements is their reaction with tertiary alcohols. Anhydrous thorium tetrachloride reacted vigorously with *tert.*-amyl alcohol to produce a thorium oxychloride. Further, when the tetra(*iso*propyl alcoholate) was treated with *tert.*-amyl alcohol in benzene a rapid evolution of olefin and alkyl chloride took place. On the other hand, when the *iso*propyl alcoholate was treated with *n*-butyl alcohol in boiling benzene the main reaction was alcohol-interchange, together with some substitution of chlorine. By crystallising the product from benzene, the new alcoholate $ThCl_4,4(Bu^nOH)$ was obtained. Similarly the ethyl alcoholate was quantitatively converted into the *iso*propyl alcoholate by alcohol-interchange.

It is now clear that although the tetrachlorides of silicon, titanium, zirconium, and thorium show a well-defined variation in reactivity towards certain alcohols (ROH; where $R = Me, Et, Pr^i$, or Bu^n) their reactivity towards the tertiary alcohols follows a uniform pattern. The following equations illustrate the remarkable variation of reactivity with the first type of alcohol:

$$\begin{aligned} SiCl_4 + 4ROH &\longrightarrow Si(OR)_4 + 4HCl \\ TiCl_4 + 3ROH &\longrightarrow TiCl_2(OR)_2,ROH + 2HCl \\ 2ZrCl_4 + 5ROH &\longrightarrow ZrCl_3(OR),ROH + ZrCl_2(OR)_2,ROH + 3HCl \\ ThCl_4 + 4ROH &\longrightarrow ThCl_4,4ROH \end{aligned}$$

In this discussion, " reactivity " means the extent of the replacement of chlorine and not the reaction velocities which are indistinguishably rapid. Bradley, Halim, and Wardlaw (*J.*, 1950, 3451) suggested that the mechanisms of these reactions involved the initial co-ordination step, $R\text{-}\overset{\delta-}{O}H \longrightarrow \overset{\delta+}{M}Cl_4$, followed by an electronic rearrangement and expulsion of chloride and hydrogen ions. The reactivities were then related to a hypothetical reactivity function, $R_M = \delta+/r_M{}^4$, where $\delta+$ is the fractional positive charge induced on the central atom by the electron-attracting chlorine atoms and r_M is the radius of the central atom. With regard to the reactions of tertiary alcohols or other alcohols containing strongly electron-releasing alkyl groups it was later suggested (Bradley and Wardlaw, *J.*, 1951, 280) that secondary reactions involving the alcohol and hydrogen chloride liberated in the primary step, $ROH + MCl_4 \longrightarrow (RO)MCl_3 + HCl$, resulted in the formation of alkyl chloride and water. This view is supported by the occurrence of simple replacement reactions (with $SiCl_4$ or $TiCl_4$) in the presence of pyridine which stops the secondary reaction. Further when pyridinium hexachlorozirconate, which does not react with alcohols, is treated with *tert.*-butyl alcohol and ammonia in the presence of pyridine, no side reaction occurs and $ZrCl(OBu^t)_3,2C_5H_5N$ is formed (Bradley, Halim, Sadek, and Wardlaw, *J.*, 1952, 2032). Moreover, it was shown (Bradley, Halim, Mehrotra, and Wardlaw, *J.*, 1952, 4960) that when zirconium chloride *iso*propoxides react with tertiary alcohols the simple replacement (alcohol-interchange) reactions occur primarily, but in the presence of excess of tertiary alcohol a secondary reaction involving the formation of alkyl chloride and water also takes place. For the monochloride $ZrCl(O\cdot CMe_3)_3$, which is " non-reactive " insofar as no primary replacement of chlorine occurs, the following tentative mechanism for the formation of secondary products was proposed:



$$ZrCl(O\cdot CMe_3)_3 + CMe_3\cdot OH \longrightarrow Me_2C(OH)(CH_2\text{-}H)\cdots Zr(O\cdot CMe_3)_3Cl \longrightarrow HO\cdot Zr(O\cdot CMe_3)_3 + HCl + CH_2{:}CMe_2$$

This mechanism should be applicable to chlorides of other Group IVA elements because the initial co-ordination of the tertiary alcohol to the central atom is always possible whilst the subsequent electronic rearrangement should be largely independent of the central atom. Therefore, the reaction of thorium tetrachloride with tertiary alcohols would be expected to follow a similar mechanism, especially as this tetrachloride is also " non-reactive " towards methyl, ethyl, and *iso*propyl alcohols. The alternative mechanism, $ThCl_4,4ROH \longrightarrow R^+ + [ThCl_4(OH),3ROH]^-$ involving the formation of the carbonium ion, is less likely for thorium compounds than for zirconium compounds because of the greater electropositive nature of thorium. The further possibility remains that tertiary alcohols are more reactive than other types of alcohol and cause a primary substitution reaction, $R^tOH + ThCl_4 \longrightarrow (R^tO\cdot ThCl_3 + HCl)$, with the thorium tetrachloride. The secondary reaction would then be the combination of hydrogen chloride and the tertiary alcohol. The greater reactivity of tertiary alcohols would be due to the increased electron density on the oxygen atom attached to the electron-releasing tertiary alkyl group.

The action of heat on $ThCl_4,4EtOH$ was also studied. The compound was heated at 100°/0·7 mm. until chloride was first detected among the volatile products. The composition of the thorium compound then approximated to $ThCl_4,2EtOH$. This was further heated under the same conditions until evolution of hydrogen chloride ceased.

From the analysis of the thorium compound it was inferred that much of the tetrachloride had been converted into thorium trichloride monoethoxide. Further heating at 170° caused decomposition, leaving an oxychloride of thorium. It appears that the alcohol in $ThCl_4$,2EtOH (involving 6-covalent thorium) is more strongly bound than in $ThCl_4$,4EtOH and this difference can be attributed to both steric and electronic effects. On steric grounds the addition of four molecules of ethyl alcohol should be less favoured than the addition of two. Moreover, in terms of electrostatic attraction between thorium and co-ordinated oxygen the combination of each additional addendum should diminish the induced positive charge on the thorium and lower the energy of co-ordination in line with the theory previously proposed (Bradley, Halim, and Wardlaw, *loc. cit.*) to explain the reactivities of Group IVA tetrachlorides with alcohol.

EXPERIMENTAL

All-glass apparatus was used and special precautions were taken to exclude moisture. The alcohols were dried and the analyses were carried out as previously described (Bradley, Saad, and Wardlaw, *J.*, 1954, 1091).

Hydrated Thorium Chloride.—Commercial hydrated thorium chloride (42·8 g.; Found: Th, 44·2; Cl, 24·3%; Cl : Th, 3·6) was dissolved in hydrochloric acid (*d* 1·18; 43 c.c.). During 15 days in a desiccator (H_2SO_4; *d* 1·84) the solution deposited a crystalline mass. After filtration and washing with hydrochloric acid (*d* 1·18) the crystals (36 g.) were dried for 2 days over sulphuric acid (*d* 1·84) (Found: Th, 42·0; Cl, 25·8. Calc. for $ThCl_4,10H_2O$: Th, 41·9; Cl, 25·6%).

Thionyl Chloride.—Technical thionyl chloride was purified by a method due to Dr. W. Rigby involving distillation first with turpentine oil (6% w/v) and then with linseed oil (1% w/v). The final water-white distillate gave no colour when heated with thorium chloride.

Dehydration of Thorium Chloride Hydrate.—(*a*) *With thionyl chloride.* Thionyl chloride (60 c.c.) was added to powdered thorium chloride hydrate (12·3 g.), and a rapid evolution of sulphur dioxide and hydrogen chloride occurred although the reactants became cool. After the reaction had subsided the system was boiled for 10 hr.; no more gaseous products could then be detected. The solid was filtered off, and gave a powder (10 g.) when dried at 60° under reduced pressure (Found: Th, 56·1; Cl, 38·2%; Cl : Th, 4·45). The solid, which smelled of thionyl chloride, was heated for 2 hr. at 90°/0·1 mm. (Found: Th, 56·5; Cl, 37·4%; Cl : Th = 4·34). In another experiment the solid *product* was dried for several hr. at 120°/0·1 mm. (Found: Th, 58·2; Cl, 39·1; Cl : Th = 4·39. $SOCl_2,5ThCl_4$ requires Th, 58·3; Cl, 39·2%).

(*b*) *By azeotropic distillation.* (i) With ethyl alcohol and benzene. Hydrated thorium chloride (13 g.) was dissolved in ethyl alcohol (400 c.c.)–benzene (400 c.c.). The solution was azeotropically distilled, a fractionating column (60 cm.; packed with Fenske helices) fitted to a Dean and Stark type of stillhead being used. Most of the water was removed as the lower layer of the ternary azeotrope of water–benzene–ethyl alcohol (10·1 c.c.) but distillation was continued until the volume of the solution had been reduced to *ca.* 250 c.c. More benzene (300 c.c.) was added and the solution concentrated by boiling until crystals appeared. Next morning the crystals (13 g.) were dried at room temperature under reduced pressure (Found: Th, 41·6; Cl, 25·6; EtO, 31·3. Calc. for $ThCl_4$,4EtOH: Th, 41·6; Cl, 25·4; EtO, 32·3%).

(ii) With *iso*propyl alcohol and benzene. Benzene (280 g.) and *iso*propyl alcohol (250 g.) were added to hydrated thorium chloride (16 g.), and the mixture azeotropically dried as in the previous experiment. In the later stages some chloride was detected in the neutral distillate. The solution was concentrated to 300 c.c. and allowed to crystallise. The crystals (17 g.) were dried at room temperature under reduced pressure. Analysis confirmed that some replacement of chloride had occurred (Found: Th, 38·1; Cl, 22·3; Pr^iO, 38·3; H_2O, 0·053%; Cl : Th, 3·86). Recrystallisation of the foregoing product from *iso*propyl alcohol gave the pure *alcoholate* (Found: Th, 37·9; Cl, 22·9; Pr^iO, 38·3. $ThCl_4,4Pr^iOH$ requires Th, 37·8; Cl, 23·1; Pr^iO, 38·5%).

Reactions of Thorium Tetrachloride with Alcohols.—(1) *With methyl alcohol.* Methyl alcohol (100 c.c.) and anhydrous thorium tetrachloride (8·9 g.) reacted vigorously. The cool solution was filtered and the filtrate evaporated to dryness at 30°/0·5 mm. The solid *alcoholate* (13·8 g.) could not be crystallised from benzene, carbon tetrachloride, or light petroleum (Found: Th, 46·0; Cl, 27·7. $ThCl_4$,4MeOH requires Th, 46·2; Cl, 28·3%).

(2) *With ethyl alcohol.* Thorium tetrachloride (7·6 g.) was dissolved in ethyl alcohol (29 g.) and the filtered solution evaporated to dryness at 60° under reduced pressure. Analysis of the solid product showed that some of the addended alcohol had dissociated during drying (Found : Th, 43·4; Cl,2 6·3; EtO, 28·2%; Cl : Th, 3·96; EtO : Th, 3·34). The thermal decomposition of the alcoholate was then examined at 100°/0·7 mm. Heating was continued until the presence of chloride in the volatile products was indicated. Analysis showed that the composition of the *product* was close to $ThCl_4,2EtOH$ (Found : Th, 50·3; Cl, 30·3; EtO, 18·9; Cl : Th, 3·93; EtO : Th, 1·93. $ThCl_4,2EtOH$ requires Th, 49·5; Cl, 30·5; EtO, 19·3%).

This product was heated at 90—100°/0·7 mm. until evolution of chloride ceased. The analysis suggested that the solid product was a mixture of thorium tetrachloride and trichloride monoethoxide (Found: Th, 52·8; Cl, 29·2; EtO, 17·4%; Cl : Th, 3·62; EtO : Th, 1·70. Calc. for $ThCl_{3\cdot62}(OEt)_{0\cdot38},1\cdot32EtOH$: Th, 52·9; Cl, 29·3; EtO, 17·4%).

In another experiment the tetra(ethyl alcoholate) was heated for 2 hr. at 170°/0·1 mm. Analysis of the resulting yellow powder confirmed decomposition to an oxychloride of thorium (Found : Th, 67·1; Cl, 26·4; EtO, 2·7%; Cl : Th, 2·58; EtO : Th, 0·2).

(3) *With* iso*propyl alcohol.* Thorium tetrachloride (15 g.) was refluxed with *iso*propyl alcohol (300 c.c.) and the solution allowed to crystallise. After filtration the crystals (19 g.) were dried at room temperature under reduced pressure. The apparent molecular weight of the *tetra-alcoholate* was determined in boiling *iso*propyl alcohol in the concentration range 0·015—0·05M (Found: Th, 38·0; Cl, 23·1; Pr^iO, 38·6%; *M*, 484. $ThCl_4,4Pr^iOH$ requires Th, 37·8; Cl, 23·1; Pr^iO, 38·5%; *M*, 614).

(4) *With 2-methylbutan-2-ol.* Thorium tetrachloride (7 g.) reacted vigorously with *tert.*-amyl alcohol (11 g.) but did not dissolve. The solid was filtered off and dried at room temperature under reduced pressure. Analysis confirmed that decomposition had occurred (Found : Th, 51·5; Cl, 13·6%; Cl : Th, 1·76).

Alcohol Interchange Experiments.—(1) *Action of* iso*propyl alcohol on the tetra*(*ethyl alcoholate*). The tetra(ethyl alcoholate) (5·8 g.) was dissolved in boiling *iso*propyl alcohol (250 c.c.), and the solution allowed to crystallise. After filtration the crystalline *tetra*(iso*propyl alcoholate*) (5·6 g.) was dried at room temperature under reduced pressure (Found : Th, 37·8; Cl, 23·0; Pr^iO, 39·1. $ThCl_4,4Pr^iOH$ requires Th, 37·8; Cl, 32·1; Pr^iO, 38·5%).

(2) *Action of* n*-butyl alcohol on the tetra*(iso*propyl alcoholate*). The tetra(*iso*propyl alcoholate) (5·2 g.), benzene (64 g.), and *n*-butyl alcohol (16·5 g.) were fractionally distilled to remove *iso*propyl alcohol as the binary azeotrope with benzene. During the concentration it was observed that the distillate contained chloride and was acidic. After removal of the solvent the white solid (4·8 g.) was dried at 30—40°/0·1 mm. Analysis confirmed that some replacement of chloride had occurred (Found : Th, 34·7; Cl, 20·3%; Cl : Th, 3·83). The foregoing product (3·2 g.) was dissolved in boiling benzene (5 g.), and the solution allowed to crystallise. After filtration and washing with benzene, the crystalline *tetra-*(n*-butyl alcoholate*) (1·97 g.) was dried at room temperature under reduced pressure (Found : Th, 34·8; Cl, 21·0. $ThCl_4,4C_4H_9{\cdot}OH$ requires Th, 34·6; Cl, 21·2%).

(3) *Action of ethylene glycol on the tetra*(iso*propyl alcoholate*). The alcoholate (7·0 g.), ethylene glycol (19 g.), and benzene (60 g.) were azeotropically fractionated. The solvent was finally removed at 115° under reduced pressure, chloride being detected in the distillate. The gummy residue (8·5 g.) was insoluble in benzene, ether, carbon tetrachloride, or light petroleum and thus could not be purified. However, analysis confirmed that replacement of chlorine had occurred and suggested that at least 5 molecules of ethylene glycol were retained as addenda (Found : Th, 31·7; Cl, 16·4%; Cl : Th, 3·38).

(4) *Action of* tert.*-amyl alcohol on the tetra*(iso*propyl alcoholate*). Benzene (20 g.) and *tert.*-amyl alcohol (10 g.) were added to the tetra(*iso*propyl alcoholate) (8·65 g.), and the mixture heated; a vigorous reaction occurred with the evolution of olefin and alkyl chloride.

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