967. *The Action of Alcohols on Zirconium Tetrachloride and Zirconium Chloride Alkoxides.*

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The reactions of zirconium tetrachloride and of zirconium chloride alkoxides with various alcohols have been examined. From the tetrachloride and methanol the equimolecular mixture of $ZrCl_3(OMe),MeOH$ and $ZrCl_2(OMe)_2$ was obtained. Alcohol interchange occurs between zirconium dichloride dialkoxides or zirconium chloride trialkoxides and primary or secondary alcohols and is a convenient means for preparing zirconium chloride alkoxides. The new compounds $ZrCl(OMe)_3$ and $ZrCl_2(OMe)_2$ were thus prepared. With tertiary alcohols and $ZrCl(OPr^i)_3,Pr^iOH$ the alcohol interchange was accompanied by a second reaction which formed alkyl halide, olefin, and water, but the new chloride tri-*tert.*-amyloxide of zirconium could be prepared by a modified procedure. The nature of the second reaction was investigated and a mechanism is proposed.

BRADLEY, HALIM, and WARDLAW (*J.*, 1950, 3450) reported that the products from the reaction between zirconium tetrachloride and ethyl alcohol were $ZrCl_3(OEt),EtOH$ and $ZrCl_2(OEt)_2$ and that the order of reactivity with ethyl alcohol of the Group IV tetrachlorides was thus: $SiCl_4 > TiCl_4 > ZrCl_4 > ThCl_4$. In view of the possibility that the reactivity of zirconium tetrachloride in such reactions may depend on the nature of the alcohol, the reactions of other alcohols with the tetrachloride have been examined.

It was found that the reaction involving methyl alcohol was exactly analogous to that involving ethyl alcohol and an equimolecular mixture of $ZrCl_3(OMe),MeOH$ and $ZrCl_2(OMe)_2$ was obtained. Attempts to separate these compounds were unsuccessful. When *n*-amyl or *iso*propyl alcohol reacted with zirconium tetrachloride it was not possible to remove the excess of alcohol, even under reduced pressure, without decomposing the product. We have recently shown (Bradley, Halim, Mehrotra, and Wardlaw, *J.*, 1952, 4609) that zirconium trichloride *iso*propoxide can be prepared by the action of excess of hydrogen chloride on zirconium *iso*propoxide in benzene:

$$Zr(OPr^i)_4,Pr^iOH + 3HCl \longrightarrow ZrCl_3{\cdot}OPr^i,2Pr^iOH + 2Pr^iOH$$

It appears therefore that the trichloride alkoxides of zirconium are intermediate in reactivity between the highly reactive tetrachloride and the unreactive dichloride dialkoxides $ZrCl_2(OR)_2$. This idea is supported by the behaviour of zirconium trichloride ethoxide with boiling *iso*propyl alcohol. Alcohol interchange occurs, but is accompanied by a slow reaction in which the trichloride alkoxide is converted into the dichloride dialkoxide.

Further investigation of the reactions of the dichloride dialkoxides and the chloride trialkoxides with various alcohols has shown that they proceed as follows:

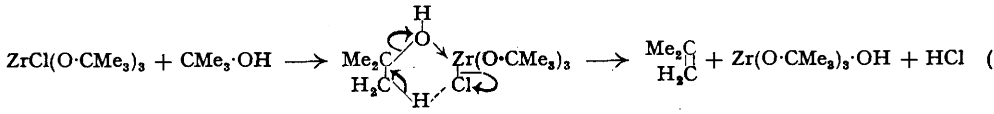
$$\begin{aligned} ZrCl_2(OEt)_2,EtOH + 3Pr^iOH &\longrightarrow ZrCl_2(OPr^i)_2,Pr^iOH + 3EtOH \\ ZrCl_2(OPr^i)_2,Pr^iOH + 2MeOH &\longrightarrow ZrCl_2(OMe)_2 + 3Pr^iOH \\ ZrCl(OEt)_3 + 4Pr^iOH &\longrightarrow ZrCl(OPr^i)_3,Pr^iOH + 3EtOH \\ ZrCl(OPr^i)_3,Pr^iOH + 3MeOH &\longrightarrow ZrCl(OMe)_3 + 4Pr^iOH \end{aligned}$$

No replacement of chloride occurred even after prolonged refluxing and it is evident that alcohol interchange alone takes place with either primary or secondary alcohols. When *tert.*-butyl or *tert.*-amyl alcohol was used the reaction showed special features. Only by employing the minimum amount of *tert.*-amyl alcohol and using benzene as solvent could the following reaction be realised:

$$ZrCl(OPr^i)_3,Pr^iOH + 3C_5H_{11}{\cdot}OH \longrightarrow ZrCl(OC_5H_{11})_3 + 4Pr^iOH \quad . \quad . \quad (1)$$

In the presence of excess of tertiary alcohol and without benzene, the reaction (1) gave way to a second reaction in which a hydrolysed zirconium compound was formed together with alkyl chloride, olefin, and water.

Further work revealed that the second reaction depended on the presence of excess of tertiary alcohol: zirconium chloride tri-*tert*.-amyloxide (1 mol.) decomposed very slowly in boiling benzene and formed olefin but no volatile chloride, whereas the subsequent addition of *tert*.-amyl alcohol (3 mols.) caused immediate decomposition with the formation of a hydrolysed zirconium compound, olefin, water, and hydrogen chloride. Evidently the excess of tertiary alcohol plays a decisive rôle and the following mechanism is tentatively suggested as the primary step in the decomposition when *tert*.-butyl alcohol is involved:



$$\mathrm{ZrCl(O{\cdot}CMe_3)_3 + CMe_3{\cdot}OH \longrightarrow Me_2C(H_2C{\cdot}H)\cdots O(H)\cdots Zr(O{\cdot}CMe_3)_3Cl \longrightarrow Me_2C{=}CH_2 + Zr(O{\cdot}CMe_3)_3{\cdot}OH + HCl} \quad (a)$$

The formation of alkyl chloride and water in the reaction involving zirconium chloride alkoxide and tertiary alcohol alone is assumed to result from the reaction between hydrogen chloride and tertiary alcohol. Mechanism (*a*) involving the cyclic transition state is similar in principle to that proposed by McElvain and Davie (*J. Amer. Chem. Soc.*, 1951, **73**, 1400) to explain de-alcoholation of carboxylic orthoesters by aluminium alkoxides. It is possible that the decompositions described above may occur by a different mechanism involving the formation of carbonium ions:

$$\mathrm{R{\cdot}OH + ZrCl(OR)_3 \longrightarrow R^+ + {}^-ZrCl(OR)_3{\cdot}OH} \quad . \; . \; . \; . \; . \; . \quad (b)$$

The formation of olefin, water, and hydrogen chloride, or alkyl chloride could be explained in terms of secondary reactions involving carbonium ions. Further work is required before it can be decided which mechanism is operative in the decomposition reaction.

The reaction between zirconium dichloride di*iso*propoxide and *tert*.-amyl alcohol was also examined. When equimolecular proportions of reactants were heated in benzene, alcohol interchange occurred but on the addition of another mol. of tertiary alcohol rapid decomposition was observed:

$$\mathrm{ZrCl_2(OPr^i)_2,Pr^iOH + CMe_2Et{\cdot}OH \longrightarrow ZrCl_2(OPr^i){\cdot}O{\cdot}CMe_2Et + 2Pr^iOH}$$
$$\mathrm{ZrCl_2(OPr^i){\cdot}O{\cdot}CMe_2Et + CMe_2Et{\cdot}OH \longrightarrow olefin + HCl, etc.}$$

This work establishes the fact that a simple alcohol interchange takes place when primary, secondary, or tertiary alcohols react with either chloride trialkoxides or dichloride dialkoxides of zirconium but that special precautions are necessary in the case of tertiary alcohols to avoid alternative reactions.

EXPERIMENTAL

All-glass apparatus was used and special precautions were taken to exclude moisture. The general methods of analysis and treatment of solvents have been previously described (Bradley, Halim, and Wardlaw, *loc. cit.*). In the alcohol interchange experiments (except when methanol was used) fractionation was carried out using a column (70 cm.) packed with Fenske helices and fitted to a total-condensation variable take-off stillhead. The composition of the distillate was estimated from its b. p. or by refractive-index measurement, and the course of the reaction thus followed.

Reaction between $ZrCl_4$ *and Methyl Alcohol.*—Methyl alcohol (120 c.c.) was added to zirconium tetrachloride (24·2 g.), a vigorous reaction occurring with evolution of hydrogen chloride. The solution was filtered and the filtrate evaporated to dryness at 110°/3 mm. A pale yellow solid (25 g.) remained which was insoluble in ether, benzene, or light petroleum, but attempts to separate the mixture were unsuccessful [Found: Zr, 37·5; Cl, 36·7; MeO, 24·8. Calc. for a mixture of $ZrCl_3{\cdot}OMe,MeOH$ (1 mol.) and $ZrCl_2(OMe)_2$ (1 mol.): Zr, 37·6; Cl, 36·6; MeO, 25·6%]. The product was soluble in methyl alcohol but could not be crystallised.

Reaction between $ZrCl_4$ *and* iso*Propyl Alcohol*.—*iso*Propyl alcohol (50 c.c.) reacted vigorously with zirconium tetrachloride (3·9 g.) and hydrogen chloride was evolved. In order to evaporate the solution to dryness the temperature was raised to 120°/0·5 mm. and some decomposition occurred (Found: Zr, 34·1; Cl, 28·4; Pr^iO, 28·2%; Cl : Zr, 2·15; Pr^iO : Zr, 1·28).

Reaction between $ZrCl_4$ and n-*Amyl Alcohol*.—*n*-Amyl alcohol (20 g.) was allowed to react with zirconium tetrachloride (1·4 g.), and the solution evaporated under reduced pressure. A viscous black oil remained after drying at 130°/1 mm. Decomposition had evidently occurred (Found: Zr, 22·5; Cl, 15·3%; Cl : Zr, 1·75).

Preparation of $ZrCl_3{\cdot}OEt,EtOH$—Although zirconium trichloride ethoxide can be prepared from zirconium tetrachloride and ethyl alcohol (Bradley, Halim, and Wardlaw, *loc. cit.*) the yield (8 g. from 29 g. of tetrachloride) is small. An improved method is now described. Zirconium tetrachloride (71·5 g., 1 mol.), suspended in benzene (250 c.c.), was treated with ethyl alcohol (28·2 g., 2 mols.) in benzene (200 c.c.), and the mixture refluxed and filtered. The filtrate was concentrated to 250 c.c. and allowed to crystallise. After four recrystallisations from benzene the final product (35·8 g.) was dried at room temp./0·1 mm. [Found: Zr, 32·0; Cl, 36·6; EtO, 31·0. Calc. for $ZrCl_3(OEt),EtOH$: Zr, 31·6; Cl, 36·8; EtO, 31·2%].

Reaction between $ZrCl_3{\cdot}OEt,EtOH$ *and* iso*Propyl Alcohol*.—Zirconium trichloride ethoxide (4·7 g.) was refluxed with *iso*propyl alcohol (120 c.c.) in the fractionating apparatus. Analysis of the distillate confirmed that alcohol interchange was taking place, but neutral chloride was also detected. The neutral chloride was probably *iso*propyl chloride formed by the reaction between hydrogen chloride and *iso*propyl alcohol. After 30 hours' heating the solution was evaporated to dryness at 100°/2 mm. and gave a white solid (4·8 g.) (Found: Zr, 31·7; Cl, 27·5; Pr^iO, 38·2%; Cl : Zr, 2·24; Pr^iO : Zr, 1·86). It is deduced from the analytical data that some replacement of chloride had occurred, *viz.*, $ZrCl_3{\cdot}OPr^i,2Pr^iOH \longrightarrow ZrCl_2(OPr^i)_2,Pr^iOH + HCl$; and that the reaction between hydrogen chloride and *iso*propyl alcohol gave the neutral chloride, detected in the distillate, and water which hydrolysed the zirconium compound.

Preparation of $ZrCl_2(OPr^i)_2,Pr^iOH$ *from* $ZrCl_2(OEt)_2,EtOH$.—The complex dichloride diethoxide (7·5 g., prepared by the method of Bradley, Halim, and Wardlaw, *loc. cit.*) was refluxed with *iso*propyl alcohol (150 c.c.) in the fractionating apparatus. About 100 c.c. of distillate (containing 2·23 g. of ethanol) was collected at a reflux ratio 10 : 1 and was replaced by pure *iso*propyl alcohol (100 c.c.). Fractionation was continued until no more ethyl alcohol could be detected in the distillate and the solution was then evaporated to dryness at 40°/2 mm. and gave a white solid (8·3 g.). No chloride was detected in the distillate. The complex zirconium dichloride di*iso*propoxide was soluble in benzene or light petroleum and crystallised from carbon tetrachloride [Found: Zr, 26·7; Cl, 20·6; Pr^iO, 52·1. Calc. for $ZrCl_2(OPr^i)_2,Pr^iOH$: Zr, 26·8; Cl, 20·8; Pr^iO, 52·2%].

Preparation of $ZrCl(OPr^i)_3,Pr^iOH$ *from* $ZrCl(OEt)_3$.—Zirconium chloride triethoxide (5·6 g., prepared by the method of Bradley, Halim, and Wardlaw, *loc. cit.*) was refluxed with *iso*propyl alcohol (150 c.c.) in the fractionating apparatus. Fractionation was continued until no more ethyl alcohol could be detected in the distillate. The solution was then concentrated to 25 c.c. and allowed to crystallise. The crystalline product (5·08 g.) was dried at room temp./2 mm. (Found: Zr, 25·3; Cl, 9·5; Pr^iO, 64·7. Calc. for $ZrCl(OPr^i)_3,Pr^iOH$: Zr, 25·1; Cl, 9·7; Pr^iO, 65·2%).

Reaction between $ZrCl_2(OPr^i)_2,Pr^iOH$ *and Methyl Alcohol*.—Methyl alcohol (150 c.c.) was added to the complex zirconium dichloride di*iso*propoxide (2 g.), and the mixture refluxed for 10 hours. The solution was rapidly evaporated to dryness at room temperature and the solid *product* (1·3 g.) dried at 100° [Found: Zr, 40·6; Cl, 31·3. $ZrCl_2(OMe)_2$ requires Zr, 40·7; Cl, 31·7%]. The product was soluble in benzene, light petroleum, or carbon tetrachloride but the solutions did not crystallise.

Reaction between $ZrCl(OPr^i)_3,Pr^iOH$ *and Methyl Alcohol*.—Methyl alcohol (120 c.c.) was added to the complex zirconium chloride tri*iso*propoxide (3·7 g.), and the mixture boiled for 5 hours. The zirconium compound disintegrated to a fine white powder but did not dissolve. The mixture of alcohols was removed by evaporation at 40°/2 mm. and a powder (2·9 g.) remained. Analysis (Found: Zr, 40·3; Cl, 14·6%) suggested that this was a mixture of zirconium chloride trimethoxide with some chloride tri*iso*propoxide. The product was refluxed for 5 hours with methyl alcohol (100 c.c.) to complete the interchange The *product* was insoluble in all the common organic solvents [Found: Zr, 41·9; Cl, 15·8. $ZrCl(OMe)_3$ requires Zr, 41·5; Cl, 16·1%].

Reaction between $ZrCl(OPr^i)_3$ and tert.-*Butyl Alcohol*.—*tert.*-Butyl alcohol (150 c.c.) was added to zirconium chloride tri*iso*propoxide (5 g.), and the mixture refluxed in the fractionating apparatus. The presence of *iso*propyl alcohol in the distillate confirmed that alcohol interchange was occurring. After 1 hour's heating some neutral chloride was detected in the distillate and thereafter the rate of formation of chloride increased. After 48 hours the b. p. of the distillate had fallen to 36° and a white solid separated. The distillate then contained olefin and neutral chloride. Analysis of the white solid (3·1 g.) (Found : Zr, 48·4; Cl, 7·1%; Cl : Zr, 0·43) showed that hydrolysis had occurred and that more than half of the original available chlorine had been replaced.

Reaction between $ZrCl(OPr^i)_3$ *and* tert.-*Amyl Alcohol.*—*tert.*-Amyl alcohol (100 c.c.) was added to zirconium chloride tri*iso*propoxide (5 g.), and the mixture refluxed in the fractionating apparatus for 72 hours. After an initial period of alcohol interchange some neutral chloride was detected in the distillate. The rate of formation of alkyl chloride increased and olefin was also detected. The white solid which separated was a hydrolysed zirconium compound (Found : Zr, 51·9; Cl, 6·3%; Cl : Zr, 0·31).

*Preparation of Zirconium Chloride Tri-*tert.*-amyloxide.*—*tert.*-Amyl alcohol (2·7 g., 3 mols.) and zirconium chloride tri*iso*propoxide (3·65 g., 1 mol.) were heated in benzene (50 c.c.) in the fractionating apparatus. During the fractionation the temperature of the solution was kept between 100° and 105° and about 7·5 c.c. of benzene–*iso*propyl alcohol azeotrope were collected. The clear solution, evaporated to dryness at 40°/0·1 mm., gave a viscous colourless liquid *alkoxide* [Found: Zr, 22·6; Cl, 8·45%; Cl : Zr, 0·96. $ZrCl(OC_5H_{11})_3$ requires Zr, 23·5; Cl, 9·1%]. No further drying of the product (which appeared to contain some solvent) was attempted because of the risk of decomposition.

The remainder (2·8 g.) of the product, dissolved in benzene (50 c.c.), was heated to 140—150° in the fractionating apparatus. During 2 hours with a high reflux ratio ($>20 : 1$) only traces of olefin and no chloride were detected in the distillate, and a small amount of solid was deposited from solution. The addition of *tert.*-amyl alcohol (3·6 g.) caused a rapid increase in the rate of formation of volatile products and the distillate separated into a lower layer (water and chloride; was strongly acidic) and an upper layer (contained no chlorine; readily decolorised bromine water). During a further 2 hours' heating the concentration of olefin, water, and hydrogen chloride in the distillate increased, as did the quantity of solid hydrolysed zirconium compound (Found : Zr, 48·8; Cl, 12·5%; Cl : Zr, 0·66) deposited from solution.

Reaction between $ZrCl_2(OPr^i)_2,Pr^iOH$ *and* tert.-*Amyl Alcohol.*—To a solution of the complex zirconium dichloride di*iso*propoxide (1·4 g., 1 mol.) in boiling benzene (150 c.c.), *tert.*-amyl alcohol (0·8 g., 2·2 mols.) was added dropwise. Fractionation was carried out with the bath-temp. at 110° During the addition of the first half of the tertiary alcohol only benzene–*iso*propyl alcohol azeotrope was collected, showing that alcohol interchange was occurring. During the addition of the second half of the tertiary alcohol a white precipitate appeared and the distillate then contained hydrogen chloride and olefin. Addition of more tertiary alcohol (2·5 g.) increased the rate of formation of precipitate whilst the distillate separated into two layers. The lower layer contained water strongly acidified with hydrogen chloride, and the upper, benzene layer contained olefin. The solid (0·7 g.) was a hydrolysed zirconium compound (Found : Zr, 44·1; Cl, 11·3%; Cl : Zr, 0·66).

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