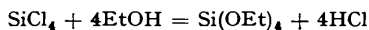


### 676. *The Chloride Ethoxides of Zirconium.*

By D. C. BRADLEY, F. M. ABD-EL HALIM, and W. WARDLAW.

Reaction of  $ZrCl_4$  with ethanol yielded the compounds  $ZrCl_3(OEt)EtOH$  (I) and  $ZrCl_2(OEt)_2$  (II). Thus the order of reactivity with ethanol is  $SiCl_4 > TiCl_4 > ZrCl_4 > ThCl_4$ . By reactions involving (I), (II), or  $Zr(OEt)_4$  with acetyl chloride the following new compounds of zirconium have been prepared:  $ZrCl_4 \cdot CH_3 \cdot CO_2Et$ ;  $ZrCl_3(OEt) \cdot CH_3 \cdot CO_2Et$ ;  $ZrCl_2(OEt)_2 \cdot EtOH$ ;  $ZrCl_2(OEt)_2 \cdot CH_3 \cdot CO_2Et$ ; and  $ZrCl(OEt)_3$ . The stability of the compounds formed by the co-ordination of a molecule of ethyl alcohol or ethyl acetate with  $ZrCl_3(OEt)$ ,  $ZrCl_2(OEt)_2$ , or  $ZrCl(OEt)_3$ , decreased as chlorine was replaced by ethoxide.

OVER a century ago Ebelmen (*Annalen*, 1846, **57**, 331) showed that ethyl alcohol reacts with silicon tetrachloride in accordance with the equation :



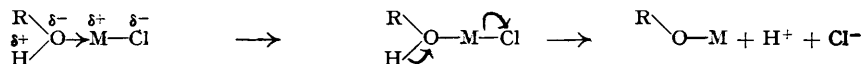
In 1936, Jennings, Wardlaw, and Way (*J.*, 1936, 637) investigated the reaction of ethyl alcohol with titanium tetrachloride and found that no simple ester was produced. Instead, from ethyl alcohol and other primary alcohols, substances of the type  $Ti(OR)_2Cl_2 \cdot ROH$  could be isolated. This indicates a striking difference in the reactivity of these two chlorides and in surveying this field of work it was surprising to discover that very little attention had been given to the reactivity of zirconium tetrachloride with aliphatic alcohols.

According to Hornberger (*Annalen*, 1876, **181**, 232) and Hinsberg (*ibid.*, 1887, **239**, 253), ethyl alcohol and zirconium tetrachloride react vigorously forming zirconium hydroxide and ethyl chloride. This indicates an entirely unexpected mechanism of reaction and it was obviously worthy of re-investigation. In doing this we discovered that it was possible to isolate two new compounds  $ZrCl_3(OEt)EtOH$  and  $ZrCl_2(OEt)_2$  from the products of the reaction of zirconium tetrachloride with ethyl alcohol provided that special precautions were taken to exclude moisture. Under these experimental conditions, no ethyl chloride could be detected. These findings fit in with the general pattern one would expect of the reactivity of the tetrachlorides of the elements in Group IVA. Thus when thorium tetrachloride reacts with alcohol the sole product of the reaction is the crystalline  $ThCl_4 \cdot 4EtOH$ .

The order of reactivity of the tetrachlorides with ethyl alcohol is now shown to be  $SiCl_4 > TiCl_4 > ZrCl_4 > ThCl_4$ , and the same order is correct for their reactivities with water. It is clear that the type of reaction between tetrachloride and alcohol changes gradually between the extremes of complete substitution, as shown by silicon tetrachloride, and simple addition (or ionisation) in the case of thorium tetrachloride. To account for this striking variation in

reactivity it is necessary to know the mechanism of the reactions involved and the physical properties of the tetrachlorides.

We think that the mechanism of the substitution reactions  $MCl_4 + nROH = M(OR)_nCl_{4-n} + nHCl$  (where  $M = Si, Ti, \text{ or } Zr$ ) is initially the co-ordination of an alcohol molecule, through a "lone pair" of electrons on the oxygen atom, thereby facilitating the repulsion of a chloride ion from an  $M-Cl$  bond and the liberation of the proton from the  $O-H$  bond.



Ridge and Todd (*J.*, 1949, 2637) recently suggested a similar mechanism for the formation of alkyl orthosilicates from silicon tetrachloride. The reactivity of the tetrachlorides is thus related to the tendency of the initial co-ordination complex to undergo the subsequent electronic rearrangement which leads to the elimination of hydrogen chloride. This tendency will be influenced by the fractional positive charge ( $\delta_M^+$ ), the atomic radius ( $r_M$ ), and the maximum covalency of  $M$  (where  $M = Si, Ti, Zr, \text{ Th}$ ). Increase in  $\delta_M^+$  favours the rearrangement, whereas increase in  $r_M$  or the maximum covalency has the opposite effect. A function of the type  $R_M = \delta_M^+ / r_M^4$  could serve as a measure for the relative reactivities of these tetrachlorides. For a given tetrachloride ( $r_M$  constant),  $\delta_M^+$  decreases as each chlorine is replaced by a less electronegative alkoxy group and the value of  $R_M$  is progressively reduced. On this basis we would expect the values of  $R_M$  in the following molecules to be of the same order:  $Si(OEt)_4$ ;  $Ti(OEt)_2Cl_2, EtOH$ ;  $Zr(OEt)Cl_3, EtOH$ ;  $ThCl_4, 4EtOH$ . In the tetrachlorides the following order should occur:  $R_{Si} > R_{Ti} > R_{Zr} > R_{Th}$ ; and this hypothesis can be tested by using the available physical data. The values of  $r_M$  (in A. units) are:  $r_{Si} 1.17$ ;  $r_{Ti} 1.36$ ;  $r_{Zr} 1.48$ ;  $r_{Th} 1.65$  (Sidgwick, "The Chemical Elements and their Compounds," Vol. I, p. xxix). The values of  $\delta_M^+$  can be assessed approximately by using the

correlation between the percentage ionic character of the bond  $M-Cl$  and the difference in the electronegativities of the atoms  $M$  and  $Cl$  (Pauling, "Nature of the Chemical Bond"). Pauling gives the following electronegativity differences:  $Si-Cl 1.2$ ;  $Ti-Cl 1.4$ ;  $Zr-Cl 1.4$ ; from which we obtain:  $\delta_{Si}^+ = 1.2e$ ;  $\delta_{Ti}^+ = \delta_{Zr}^+ = 1.6e$ . Using these values for  $R_M = \delta_M^+ / r_M^4$  we find:  $R_{Si} = 64$ ;  $R_{Ti} = 47$ ;  $R_{Zr} = 33$  (in arbitrary units). The order of the reactivity functions is clearly  $R_{Si} > R_{Ti} > R_{Zr}$  which is in accordance with experimental data. The reactivity function  $R_M$  can be considered as being derived from two terms,  $\delta_M^+ / r_M^2$  and  $1 / r_M^2$ , such that  $R_M = (\delta_M^+ / r_M^2) \times (1 / r_M^2)$ . The term  $\delta_M^+ / r_M^2$  is proportional to the "surface intensity" of induced positive charge on the atom  $M$  and influences the degree of electrostatic interaction which occurs with the initial co-ordination of an alcohol molecule to the tetrachloride. As  $r_M$  increases, more alcohol molecules can be accommodated around the central atom  $M$  and the specific effect of the positive field on each co-ordinated alcohol molecule becomes less. This effect is allowed for in the additional term  $1 / r_M^2$ .

Alternatively, the problem can be considered in terms of bond energies and heats of reaction. Sidgwick (*op. cit.*) gives the formation energies of  $M-Cl$  bonds as  $Si-Cl 85.8$ ,  $Ti-Cl 97.0$ , and  $Zr-Cl 116.9$  kcal., to which can be added a probable value for  $Th-Cl$  of 140 kcal. Although these figures are not bond dissociation energies they nevertheless suggest a marked increase in bond strength as the atomic number of the central atom increases. However, our proposed mechanism for the reactions involves the formation of ions and it would be more relevant to

compare the "ionic bond dissociation energies," *i.e.*,  $M-Cl \longrightarrow M^+ + Cl^-$ . By adding the ionisation energy ( $M \longrightarrow M^+ + e$ ) to the formation energy ( $M-Cl \longrightarrow M + Cl$ ) and subtracting the electron affinity of chlorine ( $Cl + e \longrightarrow Cl^-$ ), an approximate measure of the ionic bond dissociation energy is obtained. Syrkin and Dyatkina ("Structure of Molecules," 1950, p. 37) give the following ionisation energies (kcal.):  $Si 186.6$ ;  $Ti 156.9$ ;  $Zr 159.4$ ; and the electron affinity of chlorine as 86 kcal. Combining these figures we obtain the following ionisation bond energies (kcal.):  $Si-Cl 186.4$ ;  $Ti-Cl 167.9$ ;  $Zr-Cl 190.3$ ; which are of the same order of magnitude. We therefore infer that the "co-ordination energy" (in the process

$EtOH + MCl_4 = \begin{array}{c} Et \\ \delta^- \quad \delta^+ \quad \delta^- \\ \delta^+ \quad \delta^- \\ \text{H} \end{array} \text{O} \rightarrow MCl_4$ ) decreases as the atomic number of  $M$  increases, in line with the idea that the reactivity functions  $R_M$  (which affect the co-ordination energy) decrease in the same

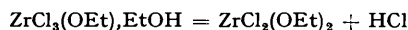
sense. When an alcohol molecule reacts with silicon tetrachloride the " co-ordination energy " is sufficient to facilitate the dissociation of both  $\overset{\delta^+}{\text{Si}}-\overset{\delta^-}{\text{Cl}}$  and  $\overset{\delta^-}{\text{O}}-\overset{\delta^+}{\text{H}}$  bonds and substitution occurs, but in the case of thorium tetrachloride the co-ordination energy is not sufficient to bring about substitution although it may be enough to release the chloride ion, *i.e.*, cause ionisation.

In concluding this discussion on the relative reactivities of the tetrachlorides of Si, Ti, Zr, and Th with ethyl alcohol we would mention a further possibility, namely, the nature of the M-Cl bonds. Thus, besides the simple variation in ionic character, there may be other more fundamental changes occurring, involving the orbital hybridisation of the bonds, which may invalidate the comparison of reactivities in terms of the simple mechanism proposed.

The solid product which is obtained from the reaction of zirconium tetrachloride with excess of ethyl alcohol is an approximately equimolecular mixture of  $\text{ZrCl}_3(\text{OEt}), \text{EtOH}$  and  $\text{ZrCl}_2(\text{OEt})_2$ . We suggest that the primary reaction is

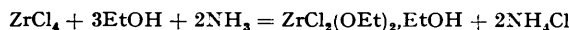


and that the  $\text{ZrCl}_2(\text{OEt})_2$  results from the decomposition

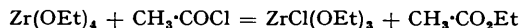


In fact, when the free ethyl alcohol in the alcoholic solution of zirconium tetrachloride was removed by azeotropic distillation with either benzene or light petroleum, the resulting solution contained only  $\text{ZrCl}_2(\text{OEt})_2$ .

When the tetrachloride and alcohol react in the presence of the appropriate amount of ammonia, the reaction proceeds as follows :

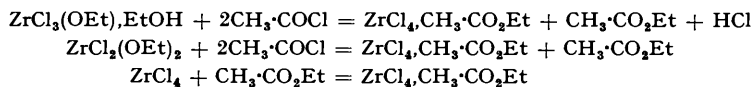


The alcohol of crystallisation can be removed from the  $\text{ZrCl}_2(\text{OEt})_2, \text{EtOH}$  by prolonged heating at  $80^\circ/0.5$  mm. It is therefore less firmly bound than when associated with  $\text{ZrCl}_3(\text{OEt}), \text{EtOH}$ . Even at  $140^\circ$  under very low pressure, the alcohol is not liberated from  $\text{ZrCl}_3(\text{OEt}), \text{EtOH}$  but decomposition occurs. The analogous compounds, with ethyl acetate as the addendum, showed a similar contrast in stability. Thus  $\text{ZrCl}_3(\text{OEt}), \text{CH}_3\cdot\text{CO}_2\text{Et}$  retained its molecule of ethyl acetate under conditions which caused the dissociation of  $\text{ZrCl}_2(\text{OEt})_2, \text{CH}_3\cdot\text{CO}_2\text{Et}$ . To complete the series of zirconium chloride ethoxides the new substance  $\text{ZrCl}(\text{OEt})_3$  was isolated without addendum, by the following reaction :

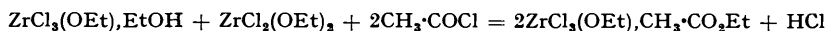


It is evident that in the series  $\text{ZrCl}_3(\text{OEt}), \text{ZrCl}_2(\text{OEt})_2, \text{ZrCl}(\text{OEt})_3$  the tendency to increase the covalency of the metal atom by the addition of either ethyl alcohol or ethyl acetate decreases as the chlorine is replaced by ethoxyl groups. A possible explanation of this phenomenon is that replacement of chlorine by ethoxyl lowers the net induced positive charge on the zirconium atom, thereby lowering the bonding energy between zirconium and the co-ordinating oxygen. This idea can be extended to account for the fact that the phenoxides  $\text{ZrCl}(\text{O}\cdot\text{C}_6\text{H}_5)_3$  and  $\text{Zr}(\text{O}\cdot\text{C}_6\text{H}_5)_4$  combine with a molecule of phenol each (Funk and Rogler, *Z. anorg. Chem.*, 1944, 252, 323), in contrast to the analogous ethoxides  $\text{ZrCl}(\text{OEt})_3$  and  $\text{Zr}(\text{OEt})_4$  which do not form addition compounds with either alcohol or ethyl acetate. We would expect the values of  $\delta_{\text{Zr}}^+$  to be greater in the phenoxy-derivatives than in the ethoxides, owing to the greater electro-negativity of the phenoxy-group.

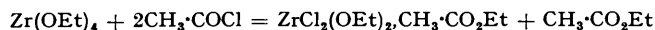
The reactions of these new zirconium compounds with acetyl chloride present some novel features. For example, in attempting to eliminate the alcohol molecule from the complex  $\text{ZrCl}_3(\text{OEt}), \text{EtOH}$ , excess of acetyl chloride was added. The product, however, proved to be the new compound  $\text{ZrCl}_4, \text{CH}_3\cdot\text{CO}_2\text{Et}$  which was also produced in the following series of reactions :



The compound  $\text{ZrCl}_3(\text{OEt}), \text{CH}_3\cdot\text{CO}_2\text{Et}$  was obtained when the requisite amount of acetyl chloride was added to the solid product from the reaction of zirconium tetrachloride with ethyl alcohol, in accordance with the equation :



When acetyl chloride (2 mols.) was added to zirconium tetraethoxide (1 mol.) the compound  $\text{ZrCl}_2(\text{OEt})_2, \text{CH}_3 \cdot \text{CO}_2\text{Et}$  was formed :



In many co-ordination compounds zirconium shows a covalency of 6 or 8, but, in the series of new compounds we have described, the empirical formulæ suggest an apparent covalency of 5 although a detailed study of structure may disclose a true covalency of 6.

#### EXPERIMENTAL.

*Apparatus.*—Special precautions were taken to exclude moisture, and all-glass apparatus was used.

*Zirconium Tetrachloride.*—The finely powdered pale yellow solid gave Zr, 39.0% (Calc. for  $\text{ZrCl}_4$  : Zr, 39.14%).

*Ethyl Alcohol.*—Absolute alcohol was dried over magnesium ethoxide and fractionally distilled.

*Acetyl Chloride.*—Redistilled grade was treated with phosphorus pentachloride and fractionally distilled.

*Ethyl Acetate.*—"AnalaR" grade was washed with calcium chloride solution, then with water, and finally redistilled after being dried over anhydrous potassium carbonate.

*Other Solvents.*—Carbon tetrachloride was distilled over phosphoric oxide. Benzene ("AnalaR") and light petroleum (b. p. 95—110°) were dried over sodium wire and distilled.

*Analytical Methods.*—Zirconium was determined gravimetrically as zirconium oxide.

Chlorine was determined volumetrically (Volhard's method) or gravimetrically as silver chloride.

Ethoxide determinations were carried out volumetrically, using a back-titration method. A weighed sample was added to a measured amount (excess) of chromic acid (*n*-potassium dichromate in 12.5% sulphuric acid) in a closed vessel. After 2 hours, the unchanged dichromate was determined iodometrically. Under these conditions ethyl alcohol is quantitatively converted into acetic acid (Adams and Nicholls, *Analyst*, 1929, **54**, 2).

Carbon and hydrogen analyses were carried out by Drs. Weiler and Strauss, Oxford.

*Reaction between  $\text{ZrCl}_4$  and Ethyl Alcohol.*—Ethyl alcohol (20 c.c.), added to zirconium tetrachloride (7.6 g.), reacted vigorously, with liberation of hydrogen chloride. The solution was refluxed for 30 minutes and then filtered, and the filtrate concentrated under reduced pressure to a viscous yellow liquid, which on being heated at 100°/1 mm. solidified (yield 9.1 g.) [Found : Zr, 33.6; Cl, 32.2%; Cl/Zr, 2.46. Calc. for  $\text{ZrCl}_3(\text{OEt}), \text{EtOH}$  (1 mol.) +  $\text{ZrCl}_2(\text{OEt})_2$  (1 mol) : Zr, 33.7; Cl, 32.8%].

*Isolation of  $\text{ZrCl}_3(\text{OEt}), \text{EtOH}$ .* The foregoing solid was dissolved in boiling benzene (15.9 g.). Pale yellow crystals separated on cooling. By using a decantation technique, the crystals (4.3 g.) were washed with benzene (Found : Zr, 28.3; Cl, 30.6%; Cl/Zr, 2.78). After crystallising five times from benzene, a colourless *product* (0.72 g.) was obtained [Found : Zr, 31.9; Cl, 36.7; EtO, 31.6.  $\text{ZrCl}_3(\text{OEt}), \text{EtOH}$  requires Zr, 31.6; Cl, 36.8; EtO, 31.2%]. From the mother-liquors, a solid (3.7 g.) was obtained which consisted mainly of  $\text{ZrCl}_2(\text{OEt})_2$  [Found : Zr, 33.3; Cl, 27.9%; Cl/Zr, 2.16. Calc. for  $\text{ZrCl}_2(\text{OEt})_2$  : Zr, 36.2; Cl, 28.1%].

In a duplicate experiment, ethyl alcohol (41.5 g.) was added to zirconium tetrachloride (28.9 g.) and from the solution a solid (33.2 g.) was obtained which gave, on analysis : Cl/Zr, 2.50. This solid was fractionally crystallised and gave a crop of needle-shaped crystals (8 g.) (Found : Zr, 32.0; Cl, 36.6; EtO, 31.0%).

*Properties of  $\text{ZrCl}_3(\text{OEt}), \text{EtOH}$ .* The solid dissolved instantly in water, to give a clear acidic solution. It was very soluble in ethyl alcohol but sparingly soluble in cold benzene although a *ca.* 10% w/w solution was obtained on boiling.

(a) *Action of heat.* A sample heated to 140°/10<sup>-4</sup> mm. in a "molecular still" did not sublime, but evidence of decomposition was afforded by a steady rise in pressure (0.01 mm. at 133°) and confirmed by analysis (Found : Zr, 38.7; Cl, 28.8; EtO, 26.4%; Cl/Zr, 1.91; EtO/Zr, 1.40). When it was heated at 160° further loss of both ethoxide and chloride occurred.

(b) *Active-hydrogen determination.* Methylmagnesium iodide in *n*-butyl ether was added to  $\text{ZrCl}_3(\text{OEt}), \text{EtOH}$  under dry nitrogen. A vigorous reaction occurred which reached completion within 30 minutes. 0.516 g. of the substance gave 38.5 c.c. (at N.T.P.) of gas [ $\text{ZrCl}_3(\text{OEt}), \text{EtOH}$  requires 40.0 c.c.].

(c) *Action of excess of acetyl chloride.* Acetyl chloride (15 c.c.), added to  $\text{ZrCl}_3(\text{OEt}), \text{EtOH}$  (1.3 g.), caused a vigorous reaction. Removal of unchanged acetyl chloride under reduced pressure gave the *product* as a yellow oil which solidified slowly at 90—100°/1 mm. (Found : Zr, 27.3; Cl, 40.1; EtO, 10.5%; Cl/Zr, 3.81; EtO/Zr, 0.78.  $\text{ZrCl}_4, \text{CH}_3 \cdot \text{CO}_2\text{Et}$  requires Zr, 28.4; Cl, 44.1%). Although  $\text{ZrCl}_3(\text{OEt}), \text{CH}_3 \cdot \text{COCl}$  has the same empirical formula as  $\text{ZrCl}_4, \text{CH}_3 \cdot \text{CO}_2\text{Et}$ , the latter seemed the more probable formula for this product because the substance dissolved in water and gave a clear acidic solution which smelled strongly of ethyl acetate. In addition,  $\text{ZrCl}_3(\text{OEt}), \text{CH}_3 \cdot \text{COCl}$  requires EtO/Zr, 1.00, whereas the ratio for  $\text{ZrCl}_4, \text{CH}_3 \cdot \text{CO}_2\text{Et}$  depends on the hydrolysis of ethyl acetate : a "blank" determination with pure ethyl acetate and chromic acid reagent, at room temperature, gave *ca.* 55% hydrolysis. Hence  $\text{ZrCl}_4, \text{CH}_3 \cdot \text{CO}_2\text{Et}$ , which evolved heat when hydrolysed, would be expected to give EtO/Zr, 0.55—1.00 (Found : 0.78). The formula  $\text{ZrCl}_4, \text{CH}_3 \cdot \text{CO}_2\text{Et}$  was confirmed by preparing the same compound directly by the addition of ethyl acetate to zirconium tetrachloride.

*Preparation of  $ZrCl_4 \cdot CH_3 \cdot CO_2Et$  by Other Methods.*—(a) From  $ZrCl_2(OEt)_2$  and excess of acetyl chloride. Acetyl chloride (40 c.c.) was added to  $ZrCl_2(OEt)_2$  (9.6 g.) and, after the mixture had refluxed for 10 minutes, the excess of acetyl chloride was removed under reduced pressure. The brown solid obtained was recrystallised four times from benzene and gave large colourless crystals (Found: Zr, 28.6; Cl, 43.7%).

(b) *Addition of ethyl acetate to  $ZrCl_4$ .* Ethyl acetate (100 c.c.) was added to zirconium tetrachloride (6.5 g.). A vigorous reaction occurred but no hydrogen chloride was evolved. The yellow solution obtained by filtration was concentrated under reduced pressure to a brown solid (9.8 g.) which was recrystallised twice from benzene. The colourless crystalline product was identical in crystalline form with the material obtained in the previous experiment (Found: Zr, 28.5; Cl, 43.9; C, 15.0; H, 2.6.  $ZrCl_4 \cdot CH_3 \cdot CO_2Et$  requires Zr, 28.4; Cl, 44.1; C, 14.9; H, 2.5%).

*Preparation of  $ZrCl_3(OEt) \cdot CH_3 \cdot CO_2Et$ .*—Acetyl chloride (4.1 g.) in benzene (24.7 g.) was added to an equimolecular mixture of  $ZrCl_3(OEt) \cdot EtOH$  and  $ZrCl_2(OEt)_2$  (14.2 g.) in benzene (50 c.c.) and refluxed for 15 minutes. The solution was concentrated to half bulk and then deposited a mass of crystals. After being recrystallised several times from benzene, the colourless product (2.9 g.) was dried at  $100^\circ/1$  mm. [Found: Zr, 28.4; Cl, 32.0; EtO, 20.7; C, 21.3; H, 3.9.  $ZrCl_3(OEt) \cdot CH_3 \cdot CO_2Et$  requires Zr, 27.6; Cl, 32.2; C, 21.8; H, 4.0%].

*Preparation of  $ZrCl_2(OEt)_2$ .*—(a) *In benzene solution.* Ethyl alcohol (20 c.c.) was added to zirconium tetrachloride (4.05 g.), and the solution boiled for 30 minutes and filtered. Benzene (300 c.c.) was added to the filtrate, and the free alcohol removed slowly by azeotropic distillation at  $100^\circ$ . A 50-cm. column packed with Fenske helices was used, with a Whitmore-Lux pattern total-condensation variable-take-off stillhead. The distillate was contaminated with hydrogen chloride. The solution was concentrated under reduced pressure but failed to give crystals. On evaporation to dryness *zirconium dichloride diethoxide* was obtained as a solid which was dried at  $100^\circ/1$  mm. [Found: Zr, 36.1; Cl, 26.6%; Cl/Zr, 1.87.  $ZrCl_2(OEt)_2$  requires Zr, 36.2; Cl, 28.1%]. The solid was very soluble in ethyl alcohol, benzene, or carbon tetrachloride. It was sparingly soluble in light petroleum.

(b) *In light petroleum solution.* To zirconium tetrachloride (1.0 g.), suspended in light petroleum (400 c.c.; b. p.  $95-110^\circ$ ), ethyl alcohol (5.7 g.) was added and the mixture boiled. Two liquid layers resulted but on azeotropic removal of free ethyl alcohol a single layer remained. Small clumps of crystals were deposited on cooling (Found: Zr, 36.1; Cl, 27.3%).

*Preparation of  $ZrCl_2(OEt)_2 \cdot EtOH$ .*—Zirconium tetrachloride (8.13 g.) was added slowly to a solution of ammonia (1.2 g.) in ethyl alcohol (37.0 g.), and the mixture refluxed for 1 hour and filtered cold. The filtrate was evaporated to dryness under reduced pressure and the pale yellow solid (10 g.) extracted with carbon tetrachloride (50 c.c.) and filtered at the boiling point. The filtrate was concentrated and induced to crystallise. The product obtained after recrystallisation from carbon tetrachloride was dried at  $80^\circ/1$  mm. (Found: Zr, 31.8; Cl, 24.2; EtO, 41.8%; Cl/Zr, 1.98; EtO/Zr, 2.58). The analytical values suggested that the compound corresponded to  $ZrCl_2(OEt)_2 \cdot EtOH$  from which part of the alcohol had been removed. From the mother-liquors more solid was obtained and this was recrystallised four times from carbon tetrachloride. The colourless crystalline product was dried at  $30^\circ/3$  mm. [Found: Zr, 30.95; Cl, 23.7; EtO, 44.0.  $ZrCl_2(OEt)_2 \cdot EtOH$  requires Zr, 30.6; Cl, 23.8; EtO, 45.3%].

*Preparation of  $ZrCl_4(OEt)_2 \cdot CH_3 \cdot CO_2Et$ .*—Acetyl chloride (1.74 g., 2 mols.) in benzene (10 g.) was added to zirconium tetraethoxide (3.0 g., 1 mol.) and the mixture refluxed for 30 minutes. The solution was concentrated under reduced pressure until solid appeared. After recrystallisation from benzene, the product (colourless needles) (2.8 g.) was dried at  $40-50^\circ/3$  mm. [Found: Zr, 27.1; Cl, 21.0.  $ZrCl_4(OEt)_2 \cdot CH_3 \cdot CO_2Et$  requires Zr, 26.8; Cl, 20.8%].

*Action of heat.* The foregoing product was heated for 6 hours at  $80^\circ/0.5$  mm. Analysis of the resulting gummy solid (1.6 g.) showed that the original substance was losing its ethyl acetate [Found: Zr, 31.5; Cl, 24.15; EtO, 34.7%; Cl/Zr, 1.97; EtO/Zr, 2.24.  $ZrCl_4(OEt)_2 \cdot \frac{1}{2} CH_3 \cdot CO_2Et$  requires Zr, 30.8; Cl, 23.8%].

*Preparation of  $ZrCl(OEt)_3$ .*—Acetyl chloride (0.52 g.) in benzene (6.6 g.) was added to zirconium tetraethoxide (1.8 g.) in benzene (50 c.c.), and the mixture refluxed for 15 minutes. The solution was evaporated to dryness under reduced pressure and gave solid *zirconium chloride triethoxide* (1.8 g.) which could not be crystallised from benzene, carbon tetrachloride, or light petroleum [Found: Zr, 34.7; Cl, 14.25; EtO, 49.9.  $ZrCl(OEt)_3$  requires Zr, 34.8; Cl, 13.5; EtO, 51.6%].

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