62. *Zirconium Alkoxides.*

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From the reaction between sodium ethoxide and zirconium tetrachloride in ethyl alcohol a complex sodium zirconium ethoxide has been isolated, but its composition does not accord with the formula $NaH[Zr(OEt)_6]$ reported by Meerwein and Bersin. Zirconium alkoxides have been prepared by treating solutions of zirconium tetrachloride in appropriate alcohols with anhydrous ammonia. The products are impure owing to hydrolysis which becomes very marked when secondary and tertiary alcohols are used. The cause of this hydrolysis is discussed. Ester-interchange has been successfully used for the preparation of various types of zirconium alkoxide. Tentative views are advanced to account for the interesting variation of the volatilities of zirconium alkoxides with structure of the alkyl group.

The reaction between zirconium tetrachloride and sodium ethoxide in ethyl alcohol presents some unusual features. Thus, Meerwein and Bersin (*Annalen*, 1929, **476**, 113) reported that zirconium tetraethoxide was not obtained directly owing to the formation of a complex sodium derivative to which the formula $NaH[Zr(OEt)_6]$ was assigned :

$$ZrCl_4 + 5NaOEt + EtOH = NaH[Zr(OEt)_6] + 4NaCl$$

These authors obtained zirconium tetraethoxide by the reaction :

$$NaH[Zr(OEt)_6] + HCl = Zr(OEt)_4 + NaCl + 2EtOH$$

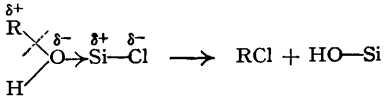
In addition, they recorded that zirconium tetraethoxide reacted with sodium ethoxide in accordance with the equation :

$$Zr(OEt)_4 + NaOEt + EtOH = NaH[Zr(OEt)_6]$$

Analogous reactions were described involving methyl alcohol in place of ethyl alcohol. We have re-investigated some of these reactions but have been unable to confirm the results of Meerwein and Bersin. However, we have found that zirconium ethoxide is readily prepared when alcohol and zirconium tetrachloride interact in the presence of ammonia. Further, this method has been successfully applied to the preparation of other zirconium alkoxides where R in the following equation is *n*-propyl, *n*-butyl, or *n*-amyl :

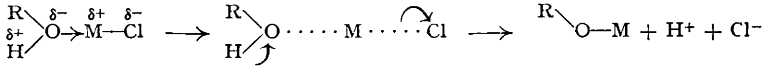
$$ZrCl_4 + 4ROH + 4NH_3 \longrightarrow Zr(OR)_4 + 4NH_4Cl$$

When secondary alcohols are used the products are appreciably hydrolysed, whilst attempts to use this method with tertiary alcohols failed. A survey of the literature disclosed that similar observations had been made in experiments designed to prepare alkoxides of silicon and titanium (Ridge and Todd, *J.*, 1949, 2637; Speer, *J. Org. Chem.*, 1949, **14**, 655). It is evident that the structure of the alcohol has a controlling influence on the degree of hydrolysis of the product resulting from the reaction of the alcohol with $SiCl_4$, $TiCl_4$, or $ZrCl_4$. Ridge and Todd (*loc. cit.*) accounted for the formation of alkyl chloride when silicon tetrachloride reacted with alcohols containing $(+I)$ alkyl groups by suggesting that the $\overset{\delta+}{R}$—$\overset{\delta-}{O}$ bond was broken, *i.e.* :



We believe the splitting of the R–OH bond to be less probable than the liberation of the proton from RO–H, even in the case of tertiary alcohols, and suggest an alternative explanation.

If it is assumed that the mechanism of the substitution reactions of these tetrachlorides is always of the following type (cf. Bradley, Halim, and Wardlaw, *J.*, 1950, 3451) :



then the hydrolysis will be caused by the water liberated in the secondary reaction between hydrogen chloride and the alcohol. The experimental facts are readily explicable on this basis as it is well known that the reaction rates of alcohols with hydrogen chloride are in the order: tertiary > secondary > primary.

In addition, we find that tertiary alkoxides of both silicon and titanium have been successfully prepared from the appropriate tetrachloride and alcohol in the presence of a tertiary base which minimises the concentration of hydrogen chloride. For example, the compounds $Si(OR)Cl_3$, $Si(OR)_2Cl_2$, and $Si(OR)_3Cl$ (where R = *tert.*-butyl or *tert.*-amyl) were prepared by Miner, Bryan, Holysz, and Pedlow (*Ind. Eng. Chem.*, 1947, **39**, 1368), from appropriate amounts of pyridine, silicon tetrachloride, and tertiary alcohol:

$$SiCl_4 + 2ROH + 2C_5H_5N \longrightarrow Si(OR)_2Cl_2 + 2C_5H_5N,HCl$$

Similarly, Cullinane and Chard (*Nature*, 1949, **164**, 710) reported the preparation of titanium tetra-*tert.*-butoxide from titanium tetrachloride by a method involving the use of pyridine followed by ammonia. We are exploring the possibilities of preparing zirconium alkoxides by using bases other than ammonia.

Zirconium alkoxides exhibit the interesting property of ester interchange when treated with alcohols:

$$Zr(OR)_4 + 4R'OH \rightleftharpoons Zr(OR')_4 + 4ROH$$

This presents possibly the best general method for the preparation of pure zirconium alkoxides. Both the tetraethoxide and the tetra*iso*propoxide can be obtained pure for use as starting materials. The impure zirconium tetraethoxide, prepared by the ammonia method, can be purified by fractional crystallisation from benzene. The impure zirconium *iso*propoxide, prepared either by the direct ammonia method or from the impure ethoxide by ester interchange, is readily purified by crystallisation from *iso*propyl alcohol as the complex $Zr(OPr^i)_4,Pr^iOH$ (I). This compound was converted into other zirconium alkoxides by treatment with the following alcohols: methyl, ethyl, *n*-butyl, *sec.*-butyl, *tert.*-butyl. The range of alcohols used indicates the scope of the ester interchange reaction.

The new zirconium alkoxides show a striking variation in physical properties. It is convenient to separate them into three groups depending on whether the alkyl group is primary, secondary, or tertiary.

(1) Primary alkoxides. Zirconium tetramethoxide and tetraethoxide are white microcrystalline solids sparingly soluble in organic solvents. As the normal hydrocarbon chain is lengthened, the zirconium alkoxides change gradually from the crystalline $Zr(OEt)_4$ to the viscous liquid $Zr(OC_5H_{11}\text{-}n)_4$. These alkoxides showed little variation in volatility and sublimed between 120° and 160° under *ca.* 10^{-4} mm. pressure.

(2) Secondary alkoxides. Zirconium tetra*iso*propoxide, obtained by heating the crystalline complex (I) under reduced pressure, was a glassy solid readily soluble in organic solvents. It softened over the range 105—120° to a liquid which distilled at 160°/0·1 mm. and was clearly much more volatile than the primary alkoxides. The crystalline complex (I) melted at 138—141° and was sparingly soluble in *iso*propyl alcohol at room temperature. The tetra-*sec.*-butoxide was a gum which could be crystallised from *sec.*-butyl alcohol presumably as the addition compound $Zr(OBu^s)_4,Bu^sOH$, but the latter was very soluble in organic solvents and readily parted with its alcohol on being dried.

(3) Zirconium tetra-*tert.*-butoxide is strikingly different from any of the other alkoxides, being a colourless mobile liquid boiling at 75—76·5°/1·7 mm. and burning with a yellow flame. It was first prepared by the action of heat on the solid hydrolysed product obtained from the tetra*iso*propoxide by ester interchange. Using the boiling points obtained at two pressures we have calculated the latent heat of vaporisation of this alkoxide to be approximately 15 kcals./g.-mol. The liquid *tert.*-butoxide was readily hydrolysed on exposure to the atmosphere.

The outstanding feature of these zirconium alkoxides is the increase in volatility as the alkyl group is changed from primary to secondary to tertiary. We hope in due course, as a result of physical measurements, to be in a position to account for these properties from a structural point of view. It seems evident that either intermolecular bonding of unusual strength or a high degree of ionic character must be responsible for the low volatility of the primary alkoxides. It is also tempting to postulate that increased branching of the alkyl group sterically prevents close intermolecular bonding between zirconium and oxygen and thus leads to increased volatility. The $(+I)$ inductive effect of the alkyl group may also play an important part since increased branching gives an increased (+*I*) effect and hence a smaller degree of ionic character in the zirconium alkoxide.

The series of alkoxides of silicon, titanium, and zirconium exhibit a remarkable change in physical properties. For example, although the alkyl orthosilicates are, as expected, only slightly less volatile than their orthocarbonate analogues, yet the comparable alkoxides of titanium and zirconium show striking decreases in volatility. The following boiling-point data serve to emphasize this: $C(OEt)_4$ 158°; $Si(OEt)_4$ 165·5°; $Ti(OEt)_4$ 142°/18 mm.; $Zr(OEt)_4$ 120°/10^{-4} mm.; $C(OPr^n)_4$ 224°; $Si(OPr^n)_4$ 225—227°; $Ti(OBu^n)_4$ 135°/0·8 mm.; $Zr(OBu^n)_4$ 160°/10^{-4} mm. The boiling points of the isomeric butyl orthotitanates, reported by Speer (*loc. cit.*), reveal an influence of chain branching on volatility similar to that which we have described in the case of the zirconium alkoxides: $Ti(OBu^n)_4$ 134—136°/0·5—1·0 mm.; $Ti(OBu^i)_4$ 141°/1 mm.; $Ti(OBu^s)_4$ 90—92°/0·5—1·0 mm.; $Ti(OBu^t)_4$ 62—63°/1 mm. The effect is just perceptible in the following boiling-point data for the isomeric dibutoxydichlorosilanes: $SiCl_2(OBu^n)_2$ 94°; $SiCl_2(OBu^n)(OBu^t)$ 83°; $SiCl_2(OBu^s)(OBu^t)$ 80°; $SiCl_2(OBu^t)_2$ 70°, all at 15 mm. pressure (calculated from data given by H. W. Post in "Organic Silicon Compounds," Reinhold, 1949).

The important features which emerge from this preliminary survey are: (i) that the increases in boiling points of alkoxides containing a given *n*-alkyl group, when the central atom changes from silicon to titanium to zirconium, are much greater than is expected on the simple basis of increases in molecular weight; (ii) that the increase in volatility resulting from branching of the alkyl groups, in isomeric alkoxides, is common to the alkoxides of these elements but the magnitudes of this effect are in the order, Zr > Ti > Si. These points suggest that striking differences can be expected in either the degree of molecular complexity or the amount of ionic character in the orthoesters (alkoxides) of silicon, titanium, and zirconium.

EXPERIMENTAL.

Special precautions were taken to exclude moisture and all-glass apparatus was used.

Chemicals.—Zirconium tetrachloride was a pale yellow powder (Found: Zr, 39·0. Calc. for $ZrCl_4$: Zr, 39·1%).

Methyl and ethyl alcohols were dried over the respective magnesium alkoxide and then fractionally distilled. Other alcohols were dried over the appropriate aluminium alkoxide and fractionally distilled.

Benzene (AnalaR) was dried over sodium wire and distilled.

Analytical Methods.—Zirconium and chloride were determined gravimetrically as zirconium oxide and silver chloride respectively.

Sodium was determined, after removal of zirconium, by evaporating the filtrate to dryness and converting the residue into either sodium chloride or sodium sulphate.

The oxidation method, described previously (Bradley, Halim, and Wardlaw, *loc. cit.*), was used for ethoxide and *iso*propoxide determinations.

The same reagent was used for determining methoxide or *sec.*-butoxide, but the method was modified as follows:

(i) Methoxide. The reactants, after being kept for 2 hours at room temperature, were heated until effervescence ceased and the formation of carbon dioxide was thus complete.

(ii) *sec.*-Butoxide. The reactants were kept for 1 hour. Trial experiments on pure substances indicated that high results were otherwise obtained.

Analyses for carbon and hydrogen were carried out by Messrs. Weiler and Strauss, Oxford.

(a) *Reactions between Sodium Ethoxide and Zirconium Tetrachloride.*—The conditions recorded by Meerwein and Bersin (*loc. cit.*) were closely followed. Zirconium tetrachloride (10 g., 1 mol.) was dissolved in ethyl alcohol (35 c.c.) and to this solution sodium ethoxide solution [4·3 g. (4·5 atoms) of sodium in 75 c.c. of alcohol] was slowly added, a finely divided precipitate being formed. After filtration, more sodium ethoxide (0·5 g. of sodium in 10 c.c. of ethanol) was added to the solution which was set aside for 24 hours. The crystalline product was washed with alcohol and one portion dried over sulphuric acid (*d* 1·84) in an evacuated desiccator (Found: Zr, 31·7; Na, 5·4%; Zr/Na, 1·48). The remainder of the product was recrystallised from xylene and dried under 0·5 mm. pressure {Found: Zr, 32·2; Na, 5·3; C, 31·1; H, 6·8; Zr/Na, 1·52; Cl, trace. Calc. for $NaH[Zr(OEt)_6]$; Zr, 23·6; Na, 6·0; C, 37·4; H, 8·1%}. A second crop of crystals, obtained from the alcoholic mother-liquor, was recrystallised from xylene, and the final product dried over silica gel at atmospheric pressure (Found: Zr, 32·1; Na, 5·4; C, 30·7; H, 6·8%; Zr/Na, 1·50).

In another experiment, a solution of sodium (6·4 g.) in ethanol (110 c.c.) was added to the cooled (10°) solution of zirconium tetrachloride (14·5 g.) in alcohol (54 c.c.). The reactants were heated to boiling and filtered. Addition of sodium ethoxide to the filtrate did not cause crystallisation but the original precipitate was heavily contaminated with zirconium. This precipitate was extracted with alcohol (300 c.c.) and filtered at the boiling point. The filtrate was concentrated to 100 c.c. and furnished some solid (5 g.) which was recrystallised from toluene (100 c.c.). The colourless hexagonal prisms were dried over silica gel [Found: Zr, 32·0; Na, 5·4; EtO, 55·0; Zr/Na, 1·50; EtO/Zr, 3·48. $Zr_6Na_4(OEt)_{21}(OH)_7$ requires Zr, 32·1; Na, 5·4; EtO, 55·5%].

These experiments showed that the complex *sodium* salt readily co-precipitated with the sodium chloride. The method of preparation was modified as follows: Ethyl alcohol (150 c.c.) was added to zirconium tetrachloride (18·6 g.) and the solution analysed for chloride. Enough sodium ethoxide, just to combine with this chloride, was then added. Thus, sodium ethoxide (6·15 g. of sodium in 100 c.c of ethanol) was slowly added to the zirconium tetrachloride solution. After 10 minutes' boiling, the mixture was filtered and more sodium ethoxide (sodium, 1·2 g.; ethanol, 50 c.c.) added to the filtrate which was set aside for 2 days. The precipitated sodium chloride was again contaminated with zirconium. The filtrate deposited a crystalline mass which was recrystallised from toluene, and the final product (7·7 g.) was dried under 0·1 mm. pressure at room temperature (Found: Zr, 31·7; Na, 5·3%; Zr/Na, 1·50). The alcoholic mother-liquor yielded more solid which, after recrystallising from toluene, weighed 2·5 g. and raised the overall yield of sodium zirconium ethoxide to 45%. This experiment established that during the addition of sodium ethoxide to an alcoholic solution of zirconium tetrachloride only part of the sodium combined with the chloride, and the rest was associated with zirconium.

(b) *Preparation of Zirconium Alkoxides by the Ammonia Method.*—For primary alkoxides the same general procedure was used throughout.

Zirconium tetraethoxide. Ammonia was passed into a solution of zirconium tetrachloride (52·5 g.) in ethyl alcohol (200 c.c.), giving a voluminous precipitate. The reaction is exothermic and the treatment with ammonia was continued until the solution had cooled to room temperature. Free ammonia was then removed under reduced pressure and the products were filtered off. After being washed with alcohol (50 c.c.), the residue (54 g.) had a zirconium content equivalent to 2·6% of ZrO_2. The clear filtrate was concentrated under reduced pressure and gave more ammonium chloride (the solubility of ammonium chloride in alcohols was increased in the presence of ammonia). The final filtrate was evaporated to dryness at 1 mm. and the pale yellow solid (47·3 g.) dried at 60° [Found: Zr, 35·2; EtO, 63·4; Cl, 0·25; EtO/Zr, 3·65. $Zr(OEt)_4$ requires Zr, 33·6; EtO, 66·4%]. The impure zirconium ethoxide was very soluble in benzene, carbon tetrachloride, or light petroleum. The pure *ethoxide* was obtained as follows: Impure zirconium ethoxide (13 g.) was dissolved in boiling benzene (130 c.c.) and allowed to crystallise. The finely divided crystals were separated, by means of a filter stick, from the yellow mother-liquors and recrystallised five times. The zirconium tetraethoxide (8·4 g.) thus obtained was a white microcrystalline solid (Found: Zr, 33·9; EtO, 65·9%). The pure compound was moderately soluble in boiling benzene but only sparingly soluble in hot ethyl alcohol. When heated in a "molecular still" it sublimed at 120° under 10^{-4} mm. pressure. The substance melted at 171—173° after exhibiting a transient phase change above 120° (depending on the rate of heating).

When sodium ethoxide was titrated against solutions of zirconium tetraethoxide in benzene–alcohol, sharp end-points (to thymolphthalein) were obtained after the addition of 0·5 equiv. of NaOEt per mol. of $Zr(OEt)_4$ [0·9286 g. and 0·5175 g. of $Zr(OEt)_4$ required 14·99 and 8·04 c.c. respectively of 0·111N-NaOEt. Calc. for $\frac{1}{2}$ equiv. of NaOEt: 15·38 and 8·55 c.c.]. According to Meerwein and Bersin (*loc. cit.*) zirconium ethoxide (1 mol.) required 1 equiv. of NaOEt, yet the analytical formula of our sodium zirconium ethoxide suggests that 2/3 equiv. should be required. This problem is still under investigation.

Zirconium n-*propoxide.* Zirconium tetrachloride (5·5 g.) was dissolved in *n*-propyl alcohol (120 c.c.) and the solution treated with ammonia. After removal of the ammonium chloride and solvent, an impure zirconium *n*-propoxide was obtained as a dark brown solid (4·9 g.) [Found: Zr, 31·0. Calc. for $Zr(OC_3H_7)_4$: Zr, 27·8%]. This compound could not be crystallised from benzene or carbon tetrachloride neither could it be sublimed even at 150°/10^{-4} mm.

Zirconium n-*butoxide.* The impure zirconium *n*-butoxide, isolated from the reaction of ammonia with the solution of zirconium tetrachloride (9·2 g.) in *n*-butyl alcohol (100 c.c.), was a brown gummy solid [Found: Zr, 25·8. Calc. for $Zr(OC_4H_9)_4$: Zr, 23·8%]. The product was soluble in benzene but could not be crystallised. When heated at 160°/10^{-4} mm. the product gave a translucent gummy sublimate (Found: Zr, 25·2%).

Zirconium n-*amyloxide.* Zirconium tetrachloride (9·2 g.) in *n*-amyl alcohol (100 c.c.) was treated with ammonia, and the impure zirconium alkoxide obtained as a clear, golden viscous liquid (15·3 g.) [Found: Zr, 21·7. Calc. for $Zr(OC_5H_{11})_4$: Zr, 20·7%]. The product was volatile at 160°/10^{-4} mm. and gave a viscous condensate which contained zirconium and liberated amyl alcohol when hydrolysed.

Zirconium iso*propoxide.* In preliminary experiments, two difficulties were encountered in the preparation of zirconium *iso*propoxide: (i) the complex *iso*propoxide $Zr(OPr^i)_4,Pr^iOH$, being sparingly soluble in *iso*propyl alcohol, was co-precipitated with the ammonium chloride and (ii) a considerably hydrolysed *iso*propoxide was obtained. The following procedure was evolved to minimise these disadvantages:

Zirconium tetrachloride (19·8 g.) was slowly added to *iso*propyl alcohol (125 c.c.) saturated with ammonia at 5°. After 2 hours' refluxing the products were filtered off at the boiling point. The residue (16·4 g.; theory for NH_4Cl, 18·0 g.), after extraction with hot benzene (75 c.c.), contained only a trace of zirconium. The filtrate and extracts were combined and concentrated to remove most of the *iso*propyl alcohol. More benzene (100 c.c.) was added and the solution treated with ammonia for 2 hours. The additional precipitate was removed and the filtrate evaporated to dryness at 80° under reduced pressure. The gummy solid (21·0 g.) was analysed with difficulty [Found: Zr, 31·6; C_3H_7O, 63·1; C_3H_7O/Zr, 3·09. Calc. for $Zr(OC_3H_7)_4$: Zr, 27·8; C_3H_7O, 72·2%].

The impure zirconium *iso*propoxide (19·8 g.) dissolved in boiling *iso*propyl alcohol (200 c.c.), and a mass of colourless crystals separated on cooling. The crystalline *complex* (17·2 g.) was dried at room temperature/0·5 mm. [Found: Zr, 24·1; C_3H_7O, 75·4; $Zr(OC_3H_7)_4,C_3H_7{\cdot}OH$ requires Zr, 23·5; C_3H_7O, 76·2%]. This crystallisation clearly affords a ready means of purifying the crude *iso*propoxide.

Zirconium sec.*-butoxide.* Treatment of zirconium tetrachloride (18·6 g.) in *sec.*-butyl alcohol (100 c.c.) with ammonia gave, after removal of ammonium chloride and solvent, a gummy product (19·4 g.) which was evidently considerably hydrolysed [Found: Zr, 31·9; C_4H_9O, 63·1. Calc. for $Zr(OC_4H_9)_4$: Zr, 23·8; C_4H_9O, 76·2%].

Zirconium tert.*-butoxide.* Zirconium tetrachloride, added to ammoniacal ether–*tert.*-butyl alcohol and treated for a long time with ammonia, gave a hydrolysed zirconium alkoxide which still contained chloride reactive to sodium *tert.*-butoxide. Zirconium *tert.*-butoxide was then prepared as follows:

To a solution of sodium (10·2 g.) in *tert.*-butyl alcohol (450 c.c.), zirconium tetrachloride (25·8 g.) was carefully added and the products were refluxed for 8 hours. The suspension was centrifuged and the clear mother-liquor evaporated to dryness under reduced pressure. The solid product melted at *ca.* 230° under 1 mm. pressure and a volatile liquid (5·8 g.) was collected as the bath-temperature rose to 260°. This liquid *tetra-*tert.*-butoxide* was redistilled at 75—76·5°/1·7 mm. pressure and gave a colourless mobile distillate (2·4 g.) [Found: Zr, 23·35. $Zr(OC_4H_9)_4$ requires Zr, 23·8%].

(c) *Ester-interchange Experiments.*—Because of the reversibility of ester-interchange reactions, the required alkoxide was obtained by employing a large excess of the reacting alcohol and fractionating the mixture to remove the more volatile liberated alcohol. The course of the reaction was followed by refractive-index and boiling-point measurements on the distillate. A 50-cm. column, packed with Fenske helices, was used in conjunction with a Whitmore–Lux-pattern total-condensation variable-take-off stillhead. When the liberated alcohol was less volatile than the reacting alcohol a different procedure was followed.

Preparation of zirconium iso*propoxide from zirconium ethoxide.* Impure zirconium ethoxide (20·7 g.) was refluxed with *iso*propyl alcohol (600 c.c.) at 130° for several days during which the alcohols were fractionated at a high reflux ratio. After collection of 500 c.c. of distillate, the crystals which deposited on cooling of the mixture were separated from the yellow mother-liquor. More *iso*propyl alcohol (600 c.c.) was added to the crystals and the fractionation continued. 300 c.c. of distillate were collected and the remaining solution was allowed to cool. The crystalline complex (30·2 g.) was washed twice and dried at room temperature under 1 mm. pressure (Found: Zr, 23·9; C_3H_7O, 75·8%). An active-hydrogen determination confirmed the presence of 1 mol. of *iso*propyl alcohol per atom of zirconium in the complex [Found: 0·7722 g. of compound liberated 48·2 c.c. (at N.T.P.) of gas. $Zr(OC_3H_7)_4,C_3H_7{\cdot}OH$ requires 44·5 c.c.]. The compound melted (capillary tube) at 138—141° and decomposed (loss of *iso*propyl alcohol) above 144°. When the crystalline compound (5·3 g.) was heated at 90—120°/1 mm. it melted and effervesced, leaving a liquid which set to a glassy translucent solid (4·5 g.) on cooling. *iso*Propyl alcohol was collected in the cold trap. The zirconium tetra*iso*propoxide prepared in this way was distilled at 160°/0·1 mm. A water-white viscous liquid was collected which set to a glassy solid (3·7 g.). This solid *zirconium tetra*iso*propoxide* melted over the range 105—120° [Found: Zr, 28·3; C_3H_7O, 71·15. $Zr(OC_3H_7)_4$ requires Zr, 27·8; C_3H_7O, 72·2%].

Preparation of zirconium methoxide from zirconium iso*propoxide.* Methyl alcohol (200 c.c.) was added to zirconium tetra*iso*propoxide (4·5 g.) and refluxed for 7 hours at 75°. The zirconium *iso*propoxide did not appear to dissolve but disintegrated to a fine white powder. The mixture of alcohols was evaporated under reduced pressure at 0° and the resulting white powder treated with more methyl alcohol (200 c.c.) and refluxed for 8 hours. The solid remaining after removal of the alcohols was dried at room temperature under 1 mm. pressure [Found: Zr, 43·1; MeO, 55·7; C, 21·4; H, 5·2. $Zr(OMe)_4$ requires Zr, 42·4; MeO, 57·6; C, 22·3; H, 5·6%]. The *zirconium tetramethoxide* appeared to be insoluble in methyl alcohol or benzene even at the boiling point.

Reaction of ethyl alcohol with zirconium iso*propoxide.* Ethyl alcohol (180 c.c.) was added to the complex $Zr(OPr^i)_4,Pr^iOH$ (4·6 g.) and refluxed for 12 hours. The mixture of alcohols was distilled under 1 mm. pressure at room temperature, giving impure tetraethoxide [Found: Zr, 33·3; EtO, 63.6. Calc. for $Zr(OEt)_4$: Zr, 33·6; EtO, 66·4%]. The analysis suggested that ester-interchange was not complete but the experiment confirmed the reversibility of the system:

$$Zr(OEt)_4 + 5Pr^iOH \rightleftharpoons Zr(OPr^i)_4,Pr^iOH + 4EtOH$$

Preparation of zirconium n*-butoxide from zirconium* iso*propoxide.* *n*-Butyl alcohol (100 c.c.) was added to the complex, $Zr(OPr^i)_4,Pr^iOH$ (6·4 g.) and slowly fractionated. The distillate (85 c.c.) was estimated to contain 5·7 c.c. of *iso*propyl alcohol (theor., 6·0 c.c.). The remaining solvent was distilled off under reduced pressure leaving the *tetra-*n*-butoxide* as a glassy solid [Found: Zr, 24·0. $Zr(OC_4H_9)_4$ requires Zr, 23·8%]. The product melted over the range 65—75°.

Preparation of zirconium sec.*-butoxide from zirconium* iso*propoxide.* *sec.*-Butyl alcohol (110 c.c.) was added to the *iso*propoxide complex (5·05 g.) and slowly fractionated. The reaction was estimated to be complete when 75 c.c. of distillate had been collected and the remainder of the solvent was then distilled off under reduced pressure. The gummy product was dried at 110°/0·5 mm. [Found: Zr, 25·3; C_4H_9O, 74·8. Calc. for $Zr(OC_4H_9)_4$: Zr, 23·8; C_4H_9O, 76·2%]. The zirconium tetra-*sec.*-butoxide was crystallised from *sec.*-butyl alcohol, but although the crystalline product was dried at room temperature under 1 mm. pressure it is suspected that partial loss of alcohol of crystallisation occurred [Found: Zr, 22·8; C_4H_9O, 79·8. Calc. for $Zr(OC_4H_9)_4,C_4H_9{\cdot}OH$: Zr, 19·9; C_4H_9O, 79·9%]. This compound melted at 60—70° under 0·5 mm. pressure, and at 80° was clearly losing alcohol of crystallisation.

Preparation of zirconium tert.*-butoxide from zirconium* iso*propoxide.* *tert.*-Butyl alcohol (350 c.c.) was refluxed for 12 hours with the *iso*propoxide complex (4·3 g.) and then fractionated for 23 hours. The distillate (75 c.c.) contained 2·6 g. of *iso*propyl alcohol (theor., 2·65 g.). After filtration, the solution was evaporated to dryness under reduced pressure and gave a gummy product (3 g.) (Found : Zr, 26·65%). This substance melted at 100° under 0·2 mm. pressure to a volatile liquid which distilled at 45·5—46·5° although the bath-temperature rose to 135° [Found : Zr, 22·8; C, 45·9; H, 8·8. Calc. for $Zr(OC_4H_9)_4$: Zr, 23·8; C, 50·1; H, 9·5%]. This liquid burned readily with a yellow flame, leaving a deposit of zirconium oxide. By applying the Clausius–Clapeyron equation to the temperature–vapour pressure data (1·7 mm. at 76°; 0·2 mm. at 46°) the approximate value of 15 kcals./g.-mol. was found for the latent heat of vaporisation of zirconium tetra-*tert.*-butoxide.

Reaction between Zirconium Tetrachloride and tert.*-Butyl Alcohol.*—*tert.*-Butyl alcohol (35 c.c.) was added to zirconium tetrachloride (8·8 g.). A sluggish reaction occurred with precipitation of zirconium hydroxide. After 10 minutes' refluxing, the product was distilled and *ca.* 25 g. of distillate (b.r. 40—80°) were collected. This liquid was washed with water and dried over potassium carbonate, and furnished a fraction (8·4 g.) which boiled at 45—53° (cf. *tert.*-butyl chloride, b. p. 51—52°). Thus, about 60% of the available chloride in zirconium tetrachloride was recovered as *tert.*-butyl chloride.

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