898. *Reactions of Acetyl Chloride with Zirconium Alkoxides.*

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Reactions of primary, secondary, and tertiary alkoxides of zirconium with acetyl chloride have been investigated and the following new compounds prepared: $ZrCl_4,Pr^nOAc$; $ZrCl_4,2Pr^iOAc$; $ZrCl_2(OPr^i)_2,Pr^iOH$; $ZrCl(OPr^i)_3,Pr^iOH$; and $ZrCl(OPr^i)_3$. No hydrogen chloride was evolved in reactions involving $Zr(OPr^i)_4,Pr^iOH$ and acetyl chloride even in the presence of excess of *iso*propyl alcohol, and $ZrCl_3(OPr^i),2Pr^iOH$ was obtained by treating $Zr(OPr^i)_4,Pr^iOH$ with hydrogen chloride. Radical-interchange reactions involving chloride alkoxides of zirconium are demonstrated and mechanisms of radical interchange between chlorides and alkoxides of silicon, titanium, and zirconium are discussed.

Bradley, Halim, and Wardlaw (*J.*, 1950, 3450) stated that reactions of acetyl chloride with certain new zirconium chloride ethoxides presented novel features; *e.g.*, an excess of acetyl chloride yielded the complex tetrachloride $ZrCl_4,EtOAc$: $ZrCl_2(OEt)_2 + 2AcCl \longrightarrow ZrCl_4,EtOAc + EtOAc$. This reaction has now been investigated for $Zr(OPr^i)_4,Pr^iOH$ and $Zr(OR)_4$ where R = Pr^n, *n*-octyl, $CHEt_2$, and *tert.*-amyl. Zirconium *n*-propoxide gave the crystalline complex $ZrCl_4,Pr^nOAc$, analogous to that from zirconium ethoxide. However, the *iso*propoxide furnished a crystalline substance $ZrCl_4,2Pr^iOAc$, which illustrates the important part played by the shape of the addendum (*e.g.*, ethyl benzoate forms $ZrCl_4,2EtOBz$). It was not possible to isolate a pure reaction product from acetyl chloride and zirconium *n*-octyloxide although there is little doubt that a derivative of zirconium tetrachloride was initially formed. Similarly it was deduced that for zirconium tetra-1-ethylpropoxide replacement had not exceeded the trichloride stage. Finally it was found that zirconium *tert.*-amyloxide was much less reactive towards acetyl chloride than the other alkoxides, the order of reactivity thus being $[Zr(OEt)_4$; $Zr(OPr^i)_4,Pr^iOH$; $Zr(OPr^n)_4$; $Zr(OC_8H_{17})_4] > Zr(O{\cdot}CHEt_2)_4 > Zr(O{\cdot}CMe_2Et)_4$. It is noteworthy that the more reactive *n*-alkoxides are highly associated in benzene solution whilst the unreactive *tert.*-amyloxide is monomeric.

A more detailed study revealed that zirconium chloride tri-*tert.*-amyloxide was formed much more readily than the dichloride di-*tert.*-amyloxide (see the Table where the mol. ratio of reactants is compared with the Cl : Zr ratio in the resulting zirconium compound).

AcCl : $Zr(O{\cdot}CMe_2Et)_4$	1·00	1·38	5·57	8·82
Cl : Zr in product	0·82	1·007	1·38	1·70

This is contrary to stereochemical considerations which suggest that steric hindrance should oppose the introduction of the first chlorine atom but that further substitution of chlorine should be facilitated. It is relevant that pyridinium zirconium hexachloride and *tert.*-butyl alcohol in the presence of ammonia (Bradley, Halim, Sadek, and Wardlaw, *J.*, 1951, 2032) give the monochloride $ZrCl(OBu^t)_3,2C_5H_5N$, whereas the lower primary or secondary alcohols give the tetra-alkoxides $Zr(OR)_4$. Evidently the Zr–O and Zr–Cl bonds in zirconium chloride tri-*tert.*-alkoxides possess some unusual character which confers additional stability.

In a detailed study of the reactions involving acetyl chloride and the *iso*propoxide $Zr(OPr^i)_4,Pr^iOH$, it was surprising to find that the following changes occurred quantitatively and that no hydrogen chloride was evolved from the possible side reaction between acetyl chloride and *iso*propyl alcohol.

$$Zr(OPr^i)_4,Pr^iOH + AcCl \longrightarrow ZrCl(OPr^i)_3,Pr^iOH + Pr^iOAc$$

$$Zr(OPr^i)_4,Pr^iOH + 2AcCl \longrightarrow ZrCl_2(OPr^i)_2,Pr^iOH + 2Pr^iOAc$$

$$Zr(OPr^i)_4,Pr^iOH + 3AcCl \longrightarrow ZrCl_3(OPr^i) + 3Pr^iOAc + Pr^iOH$$

The new crystalline compounds $ZrCl(OPr^i)_3,Pr^iOH$ and $ZrCl_2(OPr^i)_2,Pr^iOH$ were quantitatively obtained but the trichloride mono*iso*propoxide decomposed when dried. It is interesting to note that in two reactions above the *iso*propyl alcohol is the addendum in

preference to the *iso*propyl acetate. The apparently inert nature of the alcohol in these reactions was further emphasised when addition of acetyl chloride (2 mols.) to the complex zirconium *iso*propoxide (1 mol.) in the presence of (*a*) 1 mol. or (*b*) an excess of *iso*propyl alcohol gave the dichloride di*iso*propoxide $ZrCl_2(OPr^i)_2,Pr^iOH$ quantitatively and no hydrogen chloride was evolved. However, hydrogen chloride (in excess) reacted readily with zirconium *iso*propoxide as follows: $Zr(OPr^i)_4,Pr^iOH + 3HCl \longrightarrow ZrCl_3{\cdot}OPr^i,2Pr^iOH + 2Pr^iOH$. The absence of hydrogen chloride in reactions (*a*) and (*b*) above can thus be explained, since the compounds $Zr(OPr^i)_4,Pr^iOH$, $ZrCl(OPr^i)_3,Pr^iOH$, and $ZrCl_2(OPr^i)_2,Pr^iOH$ evidently combine with hydrogen chloride.

The stoicheiometric nature of these rapid reactions involving acetyl chloride suggested that radical interchange must occur between different chloride alkoxides. Thus in one preparation of $ZrCl(OPr^i)_3,Pr$ OH from acetyl chloride (1 mol.) and zirconium *iso*propoxide (1 mol.) the latter was added in two equal portions to the acetyl chloride. A vigorous reaction occurred during the first addition and there can be little doubt that at this stage the dichloride di*iso*propoxide $ZrCl_2(OPr^i)_2,Pr^iOH$ was formed. Nevertheless after the second addition the sole crystalline product was the monochloride $ZrCl(OPr^i)_3,Pr^iOH$. Accordingly we investigated the possibility of radical interchange and this mechanism was confirmed by the realisation of reactions which satisfied the requirements of the following equations:

$$ZrCl_3{\cdot}OEt,EtOAc + ZrCl(OEt)_3 + EtOAc \longrightarrow 2ZrCl_2(OEt)_2,EtOAc \quad . \quad (i)$$

$$ZrCl_2(OPr^i)_2,Pr^iOH + Zr(OPr^i)_4,Pr^iOH \longrightarrow 2ZrCl(OPr^i)_3,Pr^iOH \quad . \quad (ii)$$

$$ZrCl_4,2Pr^iOAc + Zr(OPr^i)_4,Pr^iOH \longrightarrow ZrCl_2(OPr^i)_2,Pr^iOH + ZrCl_2(OPr^i)_2,Pr^iOAc + Pr^iOAc \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (iii)$$

In the experiment (eqn. iii) involving the complex tetrachloride a single crystallisation gave a quantitative yield of the less soluble complex dichloride di*iso*propoxide $ZrCl_2(OPr^i)_2,Pr^iOH$.

Bradley, Hancock, and Wardlaw (*J.*, 1952, 2773) established that titanium tetrachloride readily interchanges with titanium tetra-alkoxides and it is evident that the mechanism of radical interchange must play an important part in any reaction in which chloride alkoxides of titanium or zirconium are formed [*viz.*, $MCl_4 + 3ROH \longrightarrow MCl_2(OR)_2,ROH + 2HCl$; $M(OR)_4 + AcCl \longrightarrow MCl(OR)_3 + ROAc$; $M(OR)_4 + 2HCl \longrightarrow MCl_2(OR)_2,ROH + ROH$]. It is noteworthy that radical interchanges involving silicon tetrachloride and alkyl orthosilicates only proceed slowly and at elevated temperatures and it is possible that a change in mechanism occurs on passing from silicon to titanium and zirconium. Thus a bimolecular rate-determining step (*ia*) may be involved for silicon:

$$(RO)_2ClSi \ldots . Cl \ldots . Si(OR)_3 \ldots . OR \longrightarrow {}^+SiCl(OR)_2 + SiCl(OR)_3 + RO^- \quad . \quad (ia)$$

$${}^+SiCl(OR)_2 + RO^- \longrightarrow SiCl(OR)_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (ib)$$

On the other hand the greater ionic character of Ti–Cl, Ti–OR, Zr–Cl, and Zr–OR bonds may favour the following unimolecular mechanism:

$$\left.\begin{aligned} M(OR)_4 &\rightleftharpoons {}^+M(OR)_3 + RO^- \\ MCl_2(OR)_2 &\rightleftharpoons {}^+MCl(OR)_2 + Cl^- \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (ii)$$

Mechanism (*ia*) would impose considerable steric restrictions on the interchange involving silicon compounds and this is in accord with Gerrard and Jones's results (*J.*, 1952, 1690) for reactions of silicon tetrachloride with *n*-, *iso*-, and *sec.*-butyl orthosilicate at 150° (sealed tube). Only the *n*-butyl orthosilicate interchanged with the tetrachloride: $SiCl_4 + Si(OBu^n)_4 \longrightarrow SiCl_3{\cdot}OBu^n + SiCl(OBu^n)_3$. Mechanism (ii) should be independent of steric factors and it is noteworthy that titanium tetrachloride reacts rapidly with titanium primary, secondary, or tertiary alkoxides (Bradley, Hancock, and Wardlaw, *loc. cit.*). The interchange reactions involving different central atoms, *e.g.*, $TiCl_4 + Si(OR)_4$, are now being investigated.

Experimental

All-glass apparatus was used, with precautions to exclude moisture. Methods of analysis, treatment of solvents and reagents, and preparation of zirconium chloride triethoxide and the complex $ZrCl_3$·OEt,EtOAc were reported by Bradley, Halim, and Wardlaw (*loc. cit.*). Zirconium *iso*propoxide, tetra-1-ethylpropoxide, and tetra-*tert.*-amyloxide were prepared as described by Bradley, Mehrotra, and Wardlaw (*J.*, 1952, 2027). The tetra-*n*-propoxide and tetra-*n*-octyloxide were prepared from the *iso*propoxide by alcohol interchange.

Reactions involving Zirconium Alkoxides and Excess of Acetyl Chloride.—Zirconium iso*propoxide.* Adding acetyl chloride (7·1 g., 5·5 mols.) in benzene (7·5 g.) to the complex *iso*propoxide, $Zr(OPr^i)_4$,Pr^iOH (1 mol.) caused a vigorous exothermic reaction. After removal of volatile products the solution was allowed to crystallise. The solid *product* (5·3 g.) was dried at room temperature (1 mm.) [Found: Zr, 21·0; Cl, 32·25%; *M* (cryoscopic in benzene), 496. $ZrCl_4$,$2CH_3$·$CO_2C_3H_7$ requires Zr, 20·9; Cl, 32·4%; *M*, 437].

*Zirconium tetra-*n*-propoxide.* After the vigorous reaction of acetyl chloride (2·4 g., 5·35 mols.) with zirconium tetra-*n*-propoxide (1 mol.) in benzene (10 c.c.) the solution was concentrated but did not crystallise. After evaporation to dryness the brown solid (2·1 g.) was dried at 80—100°/0·2 mm. Crystallisation from benzene (4·0 c.c.) gave a pale yellow solid (Found: Zr, 26·8; Cl, 40·6%; Cl : Zr, 3·90). It appears that the product is mainly the complex tetrachloride, $ZrCl_4$,Pr^nOAc (Calc.: Zr, 27·2; Cl, 42·3%). Further attempts to dry the compound led to decomposition.

*Zirconium tetra-*n*-octyloxide.* Acetyl chloride (1·8 g., 7 mols.) was added to zirconium tetra-*n*-octyloxide (1 mol.) in benzene (10 c.c.). After removal of excess of acetyl chloride prolonged heating (6 hours at 100°/0·1 mm.) was necessary to free the product from solvent and some decomposition occurred (Found: Zr, 22·5; Cl, 29·1%; Cl : Zr, 3·33. Calc. for $ZrCl_4$,CH_3·$CO_2C_8H_{17}$: Zr, 22·5; Cl, 34·8%).

*Zirconium tetra-*1*-ethylpropoxide.* A vigorous reaction occurred between acetyl chloride (2·7 g., 5·8 mols.) and zirconium tetra-1-ethyl propoxide in benzene (15 c.c.). After evaporation to dryness at 100°/0·1 mm. a viscous liquid (1·8 g.) was obtained (Found: Zr, 29·6; Cl, 25·0%; Cl : Zr, 2·18). Although some decomposition had occurred it is unlikely that the Cl : Zr ratio exceeded 2·5 in the initial product.

*Zirconium tetra-*tert.*-amyloxide.* (i) *Reaction with excess of acetyl chloride.* To freshly distilled zirconium *tert.*-amyloxide (6·4 g., 1 mol.) in benzene (50 c.c.), acetyl chloride (5·57 mols.) was slowly added and the solution kept at 0°. After 15 mins. the excess of chloride was removed and the solution evaporated to dryness at 40°/0·1 mm., giving a yellow powder [Found: Zr, 24·7; Cl, 13·3%; Cl : Zr, 1·38. Calc. for a mixture of $ZrCl_2(OC_5H_{11})_2$ and $ZrCl(OC_5H_{11})_3$ having Cl : Zr 1·38 : Zr, 24·75; Cl, 13·3%]. In view of the incompleteness of the previous reaction, a larger excess of acetyl chloride (8·8 mols.) was added to the amyloxide (1 mol.) in benzene (70 c.c.) and the temperature allowed to rise to *ca.* 75°. No hydrogen chloride was evolved. After 12 hours the solution was separated from a small residue and evaporated to dryness at 40°/0·5 mm., giving a brown powder (5·4 g.) [Found: Zr, 25·7; Cl, 17·0%; Cl : Zr, 1·70. Calc. for a mixture of $ZrCl_2(OC_5H_{11})_2$ and $ZrCl(OC_5H_{11})_3$ with Cl : Zr 1·70: Zr, 25·9; Cl, 17·1%].

(ii) *Equimolecular proportion of acetyl chloride.* When acetyl chloride (1·3 g., 1 mol.) was added to the amyloxide (1 mol.) in benzene (30 c.c.) the temperature rose rapidly to 40°. The excess of acetyl chloride and solvent were quickly removed and a viscous yellow liquid obtained (Found: Zr, 20·4; Cl, 6·5%; Cl : Zr, 0·82).

(iii) *Preparation of zirconium chloride tri-*tert.*-amyloxide.* Acetyl chloride (1·42 g., 1·38 mols.) was added to the amyloxide (1 mol.) in benzene (30 c.c.) and the temperature rose to 40°. Evaporation to dryness under reduced pressure at 60° gave a very viscous yellow liquid (5·3 g.) (Found: Zr, 21·1; Cl, 8·3%; Cl : Zr, 1·007).

Reactions with zirconium iso*propoxide.* (i) *Preparation of zirconium chloride tri*iso*propoxide.* Acetyl chloride (1·23 g., 1 mol.) reacted vigorously with the complex *iso*propoxide $Zr(OPr^i)_4$,Pr^iOH (1 mol.) in benzene (50 c.c.). No hydrogen chloride was detected during 1 hour's refluxing. Evaporation to dryness at room temperature (0·2 mm.) gave a white solid (5·6 g.) [Found: Zr, 25·6; Cl, 9·9; OPr^i, 64·4. $ZrCl(OPr^i)_3$,Pr^iOH requires Zr, 25·1; Cl, 9·7; OPr^i, 64·9%]. The complex *zirconium chloride tri*iso*propoxide* (4·5 g.) when heated under reduced pressure at 80—90° gave the solvate-free *compound.* The solid product (3·8 g.) was soluble in light petroleum or carbon tetrachloride [Found: Zr, 29·9; Cl, 11·6; OPr^i, 58·5. $ZrCl(OPr^i)_3$ requires Zr, 30·0; Cl, 11·7; OPr^i, 58·3%].

In another experiment zirconium *iso*propoxide (13·66 g., 1 mol.) was added in two approximately equal portions to a solution of acetyl chloride (1 mol.) in benzene (40 c.c.). During the first addition a vigorous exothermic reaction occurred in which zirconium dichloride di-*iso*propoxide was undoubtedly formed. After the addition of the remainder of the *iso*propoxide the clear solution was refluxed for 1 hour and then evaporated to dryness at room temp./0·5 mm. and gave a crystalline solid (12·8 g.) (Found: Zr, 25·8; Cl, 10·0; OPr^i, 63·8%).

(ii) *Preparations of zirconium dichloride di*iso*propoxide.* Acetyl chloride (2·9 g., 2 mols.) reacted vigorously with the complex *iso*propoxide (1 mol.) in benzene (100 c.c.) but no hydrogen chloride was evolved. The solution was refluxed for 2 hours and then evaporated to dryness at 50°/1 mm. The solid *product* (6·0 g.) crystallised from benzene or carbon tetrachloride [Found: Zr, 27·0; Cl, 20·6; OPr^i, 52·0. $ZrCl_2(OPr^i)_2,Pr^iOH$ requires Zr, 26·8; Cl, 20·8; OPr^i, 52·1%).

The same product was obtained when the reactants were mixed in the presence of additional *iso*propyl alcohol.

When acetyl chloride (4·1 g., 2 mols.), the complex *iso*propoxide (1 mol.), and *iso*propyl alcohol (1 mol.) reacted in benzene (20 c.c.), the dichloride di*iso*propoxide (8·5 g.) was isolated (Found: Zr, 26·9; Cl, 20·9%).

Acetyl chloride (4·0 g., 2 mols.), the complex *iso*propoxide (1 mol.), and *iso*propyl alcohol (9·5 mols.) reacted exothermally in benzene (10 c.c.) (no hydrogen chloride evolved), giving the dichloride di*iso*propoxide (8·8 g.) (Found: Zr, 27·1; Cl, 19·9%).

(iii) *Reaction between acetyl chloride (3 mols.) and zirconium* iso*propoxide (1 mol.).* Acetyl chloride (6·2 g.) was added to the complex *iso*propoxide (10·1 g.) in benzene (15·0 g.) and the solution set aside for 2 days, then concentrated at 30—40°/1·0 mm. but the product was still liquid (10·2 g.) after 12 hours' drying. A sample had Cl : Zr = 2·95, which showed that only a trace of hydrogen chloride had been evolved. The remainder of the liquid was heated at 105°/0·5 mm. and gave a fine powder (5·9 g.) (Found: Zr, 35·2; Cl, 24·4%; Cl : Zr, 1·78). Thus the primary reaction involved formation of zirconium trichloride *iso*propoxide which decomposed at 105° in the presence of solvent.

Preparation of Zirconium Trichloride iso*Propoxide.*—A solution of the complex zirconium *iso*propoxide (6·5 g.) in benzene (28·7 g.) was treated with excess of anhydrous hydrogen chloride. The temperature rose rapidly to 45°. Treatment with hydrogen chloride was continued until the solution had cooled to room temperature, whereupon it was evaporated at >40°, first at the water pump and then at 0·1 mm. for 8 hours. The viscous liquid was set aside and slowly deposited a crystalline *product* which was washed twice with light petroleum and dried for 5 hours at 40°/0·1 mm. [Found: Zr, 24·4; Cl, 29·3; OPr^i, 46·0. $ZrCl_3(OPr^i),2Pr^iOH$ requires Zr, 24·2; Cl, 28·2; OPr^i, 47·0%].

Radical Interchange Experiments.—(i) *Reaction between zirconium trichloride ethoxide and zirconium chloride triethoxide.* The triethoxide (2·06 g., 1 mol.) and the complex $ZrCl_3(OEt),EtOAc$ (1 mol.) were dissolved in benzene (50 c.c.), and the clear solution evaporated to dryness at 80°/2 mm. The glassy solid (4·6 g.) (Found: Zr, 32·1; Cl, 23·9. Calc. for a mixture of $ZrCl_2(OEt)_2,EtOAc$ and $ZrCl_2(OEt)_2$: Zr, 31·5; Cl, 24·4%) could not be crystallised from benzene (30 c.c.) but did so after addition of ethyl acetate [0·6 g.; sufficient to convert $ZrCl_2(OEt)_2$ into $ZrCl_2(OEt)_2,EtOAc$] and concentration to 15 c.c. The solid product (2·1 g.) was dried at room temp./0·5 mm. [Found: Zr, 27·5; Cl, 20·2. $ZrCl_2(OEt)_2,EtOAc$: Zr, 26·8; Cl, 20·8%].

(ii) *Reaction between zirconium* iso*propoxide and zirconium dichloride di*iso*propoxide.* The complex *iso*propoxide (6·4 g., 1 mol.) and complex di*iso*propoxide $ZrCl_2(OPr^i)_2,Pr^iOH$ (1 mol.) were dissolved in boiling carbon tetrachloride (40·4 g.). Crystallisation occurred after concentration to *ca.* 10 c.c. The solid product (11·4 g.) was dried at room temp./0·1 mm. for 3 hours [Found: Zr, 25·7; Cl, 9·9. Calc. for $ZrCl(OPr^i)_3,Pr^iOH$: Zr, 25·1; Cl, 9·7%].

(iii) *Reaction between zirconium* iso*propoxide and the complex zirconium tetrachloride.* The *iso*propoxide (3·1 g., 1 mol.) and the complex tetrachloride $ZrCl_4,2Pr^iOAc$ (1 mol.) were dissolved in boiling carbon tetrachloride (19·0 g.). The solution was concentrated to small bulk and allowed to crystallise. The crystals (3·0 g.) were washed with carbon tetrachloride and dried at 50°/0·1 mm. [Found: Zr, 26·5; Cl, 19·7. Calc. for $ZrCl_2(OPr^i)_2,Pr^iOH$: Zr, 26·8; Cl, 20·8%].

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