377. *The Preparation of Zirconium Alkoxides.*

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The preparation of $(C_5H_6N)_2ZrCl_6$ (C_5H_6N = pyridinium) from zirconyl chloride or zirconium tetrachloride is described. The zirconium alkoxides $Zr(OR)_4$, where R = Et, Pr^i, Bu^s, and Bu^n, were prepared by treatment of $(C_5H_6N)_2ZrCl_6$ and the alcohol (ROH) with ammonia in benzene. The complex zirconium chloride reacted with *tert.*-butyl alcohol and ammonia in pyridine and gave $ZrCl(OBu^t)_3,2C_5H_5N$. This compound was converted into the mixed alkoxide $Zr(OEt)(OBu^t)_3$ which disproportionated when heated, to give zirconium tetra-*tert.*-butoxide. $(C_5H_6N)_2Zr(OEt)Cl_5$ was obtained from the reaction between sodium ethoxide and $(C_5H_6N)_2ZrCl_6$.

Recently a new method for the preparation of zirconium alkoxides was reported (Bradley and Wardlaw, *J.*, 1951, 280) involving the treatment of alcoholic solutions of zirconium tetrachloride with ammonia :

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

The method was particularly successful in the preparation of zirconium *iso*propoxide which was readily purified by crystallisation as the complex $Zr(OPr^i)_4,Pr^iOH$. By alcohol interchange other alkoxides could be prepared from the *iso*propoxide :

$$Zr(OPr^i)_4,Pr^iOH + 4ROH \longrightarrow Zr(OR)_4 + 5Pr^iOH$$

Further work (Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 2027) has demonstrated the wide scope of this procedure. However, the ammonia method proved unsuitable for the preparation of tetra-tertiary-alkoxides. Moreover, it required the use of zirconium tetrachloride which could not be readily obtained in a high state of purity. In seeking to avoid the use of the tetrachloride attention was directed to zirconyl chloride, which is readily obtainable and stable in air. We discovered that when a solution of $ZrOCl_2,6H_2O$

in alcoholic hydrogen chloride was treated with pyridine a quantitative yield of pure $(C_5H_6N)_2ZrCl_6$ was obtained (C_5H_6N = pyridinium).

The alkoxides $Zr(OR)_4$, where R = Et, Pr^i, Bu^s, and Bu^n, were obtained in a pure state by passing ammonia into a suspension of $(C_5H_6N)_2ZrCl_6$ in a mixture of benzene and the alcohol in accordance with the reaction :

$$(C_5H_6N)_2ZrCl_6 + 4ROH + 6NH_3 \longrightarrow Zr(OR)_4 + 6NH_4Cl + 2C_5H_5N$$

In the case of the *iso*propoxide a compound having an addendum of pyridine $Zr(OPr^i)_4,C_5H_5N$ was obtained but this was converted into the alcoholate $Zr(OPr^i)_4,Pr^iOH$ by crystallisation from *iso*propyl alcohol.

With *tert.*-butyl alcohol the reaction was less vigorous and no zirconium tetra-*tert.*-butoxide was isolated. Further investigation revealed that $(C_5H_6N)_2ZrCl_6$ was soluble in pyridine and when this solution was treated with excess of ammonia in the presence of *tert.*-butyl alcohol the following reaction was realised :

$$(C_5H_6N)_2ZrCl_6 + 3Bu^tOH + 5NH_3 \longrightarrow ZrCl(OBu^t)_3,2C_5H_5N + 5NH_4Cl$$

Prolonged treatment with sodium *tert.*-butoxide failed to replace the chlorine in the zirconium complex. However, complete replacement of the chlorine was effected when the complex, dissolved in benzene and the requisite amount of ethanol, was treated with ammonia. The reaction can be expressed as follows :

$$ZrCl(OBu^t)_3,2C_5H_5N + EtOH + NH_3 \longrightarrow Zr(OEt)(OBu^t)_3 + NH_4Cl + 2C_5H_5N$$

Ethoxyzirconium tri-*tert.*-butoxide is the first recorded example of a mixed alkoxide of zirconium. When heated under reduced pressure it disproportionated and gave the required zirconium tetra-*tert.*-butoxide.

In the earlier method for preparing zirconium alkoxides (Bradley and Wardlaw, *loc. cit.*) the amount of hydrolysis which occurred depended on the type of alcohol employed and increased in the order, primary < secondary < tertiary. It was suggested that this hydrolysis arose from the water formed in the second stage in the following scheme :

$$ZrCl_4 + ROH \longrightarrow ZrCl_3(OR) + HCl \quad \ldots\ldots \quad (1)$$

$$HCl + ROH \longrightarrow RCl + H_2O \quad \ldots\ldots \quad (2)$$

It is noteworthy that in the reaction between pyridinium hexachlorozirconate, alcohol, and ammonia, where no hydrogen is present, the zirconium alkoxides formed are free from hydrolysis products even when *tert.*-butyl alcohol is employed.

Some preliminary experiments on the reaction between $(C_5H_6N)_2ZrCl_6$ and sodium ethoxide in ethanol gave interesting results. For example, when equimolecular proportions were employed the reaction took the following course :

$$(C_5H_6N)_2ZrCl_6 + NaOEt \longrightarrow (C_5H_6N)_2Zr(OEt)Cl_5 + NaCl$$

The pyridinium ethoxypentachlorozirconate could be crystallised from ethanol.

EXPERIMENTAL

Apparatus.—All-glass apparatus fitted with standard joints was used and, except for the preparation of pyridinium hexachlorozirconate, special precautions were taken to exclude moisture.

Chemicals.—Zirconyl chloride was recrystallised from hydrochloric acid (*d* 1·18) containing alcohol (to 15% v/v), and the product, after being dried over sodium hydroxide (pellets), had the composition $ZrOCl_2,6H_2O$. Commercial zirconium tetrachloride was used without further purification.

The methods for drying alcohols or solvents and for the analysis of products have previously been described (Bradley and Wardlaw, and Bradley, Mehrotra, and Wardlaw, *locc. cit.*).

Pyridinium Hexachlorozirconate.—(a) *From zirconium tetrachloride.* Zirconium tetrachloride (23 g., 1 mol.) was dissolved in absolute alcohol (150 c.c.), and the solution filtered to remove insoluble impurities. To the filtrate, saturated with hydrogen chloride, a solution of pyridine (15·7 g., 2 mols.) in alcohol (50 c.c.) was added. The crystalline product (44 g.) was dried at 80°/0·1 mm. [Found : Zr, 19·4. Cl, 45·3. Calc. for $(C_5H_6N)_2ZrCl_6$: Zr, 19·6; Cl, 45·8%].

(b) *From zirconyl chloride.* The chloride $ZrOCl_2,6H_2O$ (57 g.) was dissolved in boiling absolute alcohol (700 c.c.), and the solution saturated with hydrogen chloride. Addition of pyridine (31·4 g.) gave a mass of crystals immediately. The product (91 g.) was washed with alcohol and dried at 120°/2 mm. (Found : Zr, 19·5; Cl, 45·5%). The complex zirconium chloride is soluble in water or pyridine but insoluble in benzene or carbon tetrachloride. It is sparingly soluble in ethanol and can be crystallised from methanol without change.

Zirconium Tetraethoxide.—A suspension of pyridinium hexachlorozirconate (22·3 g.) in a mixture of ethanol (50 c.c.) and benzene (200 c.c.) was treated with ammonia until the exothermic reaction was complete. After removal of the granular precipitate, the filtrate was evaporated and gave a solid product (12 g.) which still retained pyridine (*ca.* 2%) after being dried at 120°/1·0 mm. Distillation at 180°/0·1 mm. bave pure crystalline zirconium tetraethoxide (Found : Zr, 33·9; EtO, 65·9. Calc for $C_8H_{20}O_4Zr$: Zr, 33·6; OEt, 66·4%).

Zirconium iso*Propoxide.*—A mixture of *iso*propyl alcohol (80 c.c.) and benzene (150 c.c.) was added to the complex zirconium chloride (20·5 g.), and ammonia passed into the suspension until the reaction was complete. The precipitate was removed and the filtrate evaporated; a solid (12·2 g.) remained which smelled of pyridine and had the composition $[Zr(OPr^i)_4]_2,C_5H_5N$. A portion (5·1 g.) of this *complex* was recrystallised from pyridine (12 c.c.) and the crystalline product (4·9 g.) dried at room temperature (0·5 mm.) (Found : Zr, 22·8; Pr^iO, 58·7. $C_{12}H_{28}O_4Zr,C_5H_5N$ requires Zr, 22·4; Pr^iO, 58·1%. The remainder of the original product (5 g.) was recrystallised twice from *iso*propyl alcohol (20 c.c.), and the product (3·7 g.) dried at room temperature (Found : Zr, 23·9; OPr^i, 75·5. Calc. for $C_{12}H_{28}O_4Zr,C_3H_7{\cdot}OH$: Zr, 23·6; OPr^i, 76·2%).

Zirconium Tetra-n-*butoxide.*—A suspension of the complex zirconium chloride (18 g.) in a mixture of *n*-butyl alcohol (50 g.) and benzene (200 c.c.) was allowed to react with excess of ammonia. The zirconium tetra-*n*-butoxide isolated from the products was a highly viscous substance (11·5 g.) which was distilled at 260°/0·1 mm. (Found : Zr, 24·0. Calc. for $C_{16}H_{36}O_4$: Zr, 23·8%).

Zirconium Tetra-sec.-*butoxide.*—From the reaction involving the complex zirconium chloride (16·5 g.), *sec.*-butyl alcohol (70 g.), and ammonia in benzene (200 c.c.) the zirconium tetra-*sec.*-butoxide was obtained as a viscous compound (9·5 g.) which could be distilled at 180°/0·1 mm. (Found : Zr, 23·9%).

The Complex, $ZrCl(OBu^t)_3,2C_5H_5N$.—Ammonia was passed into a solution of the complex zirconium chloride (12·5 g.) in a mixture of *tert.*-butyl alcohol (70 g.) and pyridine (100 c.c.; dried over barium oxide). The treatment with ammonia was continued for 2 hours after the products had cooled to room temperature. The filtered solution was evaporated to dryness and gave a solid *complex* (5·8 g.) which was dried at 40°/1·0 mm. (Found : Zr, 18·5; Cl, 6·9. $C_{12}H_{27}OClZr,2C_5H_5N$ requires Zr, 18·1; Cl, 7·0%). The foregoing product was treated with a solution of sodium (0·3 g.) in *tert.*-butyl alcohol (45 c.c.) at the b. p. for 2 hours; a small amount of very finely divided solid was deposited. After filtration with the aid of " Hyflo Super-cell " the solution was concentrated until crystals of sodium *tert.*-butoxide appeared. No zirconium tetra-*tert.*-butoxide was isolated from the remaining solution.

Zirconium Tetra-tert.-*butoxide.*—A solution of the complex zirconium chloride (19·4 g.) in *tert.*-butyl alcohol (50 c.c.) and pyridine (150 c.c.) was treated with excess of ammonia. After filtration and evaporation of the filtrate to dryness a white solid complex (9 g.) was obtained (Found : Zr, 18·4; Cl, 6·9%). The $ZrCl(OBu^t)_3,2C_5H_5N$ (8·0 g.) was dissolved in benzene (76 g.), and sufficient ethanol (0·8 g.) added to satisfy the requirements of the equation :

$$ZrCl(OBu^t)_3,2C_5H_5N + EtOH + NH_3 \longrightarrow Zr(OEt)(OBu^t)_3 + NH_4Cl + 2C_5H_5N$$

Ammonia was passed into the solution which became warm and gave a precipitate. After filtration and removal of solvent the chloride-free solid (4·7 g.) was dried at 40°/1 mm. (Found : Zr, 25·2. $C_{14}H_{32}O_4Zr$ requires Zr, 25·7%). The *ethoxyzirconium tri*-tert.-*butoxide* (4·5 g.) was heated under 0·1 mm. pressure and melted between 110—130°. Disproportionation occurred at 180° and zirconium tetra-*tert.*-butoxide (3·0 g.; b. p. 50°/0·2 mm.) was collected (Found : Zr, 24·1. Calc. for $C_{16}H_{36}O_4Zr$: Zr, 23·8%).

Pyridinium Ethoxypentachlorozirconate.—Sodium (0·86 g., 0·037 g.-atom) was allowed to react with ethanol (20 c.c.), and the resulting solution added dropwise to a suspension of pyridinium hexachlorozirconate (17·35 g., 0·037 g.-mol.) in ethanol (100 c.c.) at the b. p. The crystalline complex zirconium hexachloride was slowly consumed and replaced by a finely divided precipitate during 5 hours' heating. The products were allowed to cool but during the subsequent slow filtration a crystalline product separated. Accordingly the residue and filtrate were recombined and more ethanol (200 c.c.) was added. After the mixture had been refluxed for 2 hours it was cooled and filtered. The filtrate was evaporated to dryness and gave a white solid *salt* [Found : Zr, 19·0; Cl, 37·1; OEt, 9·3. $(C_5H_6N)_2Zr(OC_2H_5)Cl_5$ requires Zr, 19·2; Cl, 37·4; OEt, 9·5%].

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