809. *Structural Chemistry of the Alkoxides. Part II.* Tertiary Alkoxides of Silicon, Titanium, Zirconium, and Hafnium.*

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The tertiary alkoxides $M(O{\cdot}CMe_nEt_{3-n})_4$, $M(O{\cdot}CMe_2R)_4$, and $M(O{\cdot}CMeEtPr^i)_4$, where M = Ti or Zr; n = 0, 1, 2, or 3; and R = Me, Et, Pr^n, Pr^i, or Bu^t, have been prepared. Ebullioscopic measurements show that these compounds are monomeric. Vapour-pressure measurements on the lower tertiary alkoxides show that boiling points and latent heats increase with molecular size but entropies of vaporisation show little variation. A comparison of isomeric tertiary alkoxides reveals the effect of chain branching on volatility. Most titanium tertiary alkoxides are less volatile than their zirconium analogues while hafnium *tert.*-amyloxide is more volatile than the zirconium derivative. Hence the surprising order of volatilities, Hf > Zr > Ti, is found for the *tert.*-amyloxides. The position of silicon in this series is discussed.

In Part I * of this series it was established that the volatility of the amyloxides of titanium and zirconium depends on the structure of the amyl group. It was suggested that strong intermolecular bonding involving the central atom and oxygen is responsible for the low volatility of the straight-chain amyloxides, whilst in the *tert.*-amyloxides the screening effect of the branched amyloxide groups opposes intermolecular association and leads to greater volatility. Thus the tertiary compound is the only monomer in the zirconium series and its boiling point is close to that of the titanium analogue. It seemed reasonable to suppose that all tetra-*tert.*-alkoxides of titanium and zirconium would be monomeric, thus allowing a study to be made of the influence of molecular size on volatility whilst an examination of isomeric higher tertiary alkoxides should decide whether structural effects are still important. Further the tertiary alkoxides were considered to be suitable for

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investigating the influence of the central atom on volatility. Accordingly the series of alkoxides $M(O{\cdot}CMe_nEt_{3-n})_4$, $M(O{\cdot}CMe_2R)_4$, and $M(O{\cdot}CMeEtPr^i)_4$ were prepared and examined for the compounds where $M = Ti$ or Zr, $n = 0, 1, 2,$ or 3, and $R = Me, Et, Pr^n, Pr^i$, or Bu^t.

In ebullioscopic experiments all the compounds measured were found to be monomeric. Boiling points were measured at several pressures between 0·1 and 10·0 mm. Hg for the more volatile compounds and in all cases the data fitted straight lines of the form $\log p_{mm} = a - b/T$ in the pressure range 2—10 mm. The values for the constants a and b are listed in Table 1 together with boiling points (under 5·0 mm. pressure), latent heats of vaporisation (L_v) and entropies of vaporisation at 5·0 mm. pressure ($\Delta S_{5\cdot 0}$).

The boiling points from Table 1 are plotted against molecular weights in the Figure, and the boiling points of the higher alkoxides are given in Table 2.

It is seen that the boiling points do not increase linearly with molecular weights. Moreover, the three tertiary heptyloxides gave boiling points in the order $M(O{\cdot}CMeEtPr^i)_4 > M(O{\cdot}CEt_3)_4 > M(O{\cdot}CMe_2Bu^t)_4$, showing clearly that even in the monomeric tertiary alkoxides the effect of chain branching is still significant. An interesting point that emerges from Table 1 is that although the latent heats increase with molecular size the entropies of vaporisation are sensibly constant ($42 \pm 2{\cdot}5$ cal. mole^{-1} deg.$^{-1}$) irrespective of whether the central atom is titanium or zirconium, thus emphasising the structural similarity of these compounds.

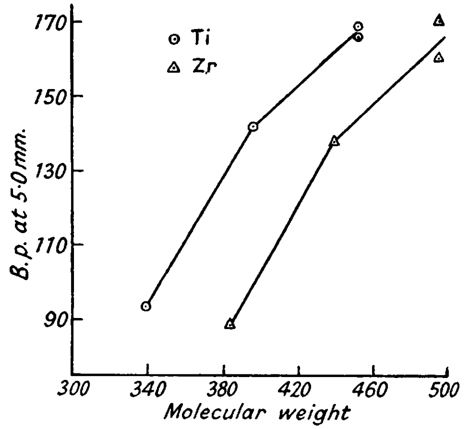

TABLE 1.

Alkoxide	B. p.	L_v (kcal./mole)	a	b	$\Delta S_{5\cdot 0}$ (cal. mole^{-1} deg.$^{-1}$)
$Ti(O{\cdot}CMe_3)_4$	93·8	14·5	9·34	3170	39·5
$Zr(O{\cdot}CMe_3)_4$	89·1	15·2	9·90	3330	42·0
$Ti(O{\cdot}CMe_2Et)_4$	142·7	16·7	9·46	3640	40·0
$Zr(O{\cdot}CMe_2Et)_4$	138·4	16·3	9·34	3550	39·5
$Ti(O{\cdot}CMeEt_2)_4$	170·4	19·0	10·1	4170	43·0
$Zr(O{\cdot}CMeEt_2)_4$	171·4	19·0	10·1	4170	43·0
$Ti(O{\cdot}CMe_2Pr^n)_4$	167·0	19·5	10·4	4270	44·0
$Zr(O{\cdot}CMe_2Pr^n)_4$	161·6	19·0	10·2	4140	44·0

TABLE 2.

Alcohol	Ti alkoxide	Zr alkoxide	Alcohol	Ti alkoxide	Zr alkoxide
$Pr^iMe_2C{\cdot}OH$	147°/0·5	133°/0·1	$Bu^tMe_2C{\cdot}OH$	163°/0·5	168°/0·5
$Et_3C{\cdot}OH$	180°/0·5	180°/0·4	$Pr^iEtMeC{\cdot}OH$	197°/1·0	194°/0·7

For a given tertiary alkoxide it is seen that there is little difference in the boiling points of the titanium and the zirconium derivative. In fact it appears that the titanium analogue often has the higher boiling point. Moreover, fractional distillation of a mixture of the tetra-*tert.*-amyloxides of zirconium and hafnium revealed that the hafnium derivative was slightly the more volatile. From general considerations it would be reasonable to expect that the order of volatilities for the tetra-*tert.*-alkoxides of silicon and the Group IVA elements would be $Si(OR)_4 > Ti(OR)_4 > Zr(OR)_4 > Hf(OR)_4 > Th(OR)_4$. However, it appears that for the *tert.*-amyloxides the actual order of volatilities is Hf>Zr>Ti. The position of silicon in this series is thus of exceptional interest particularly in view of the fact that the preparation of a tetra-*tert.*-alkoxide of this element has not yet been reported. Miner, Bryan, Holysz, and Pedlow (*Ind. Eng. Chem.*, 1947, **39**, 1368) described the preparation of $SiCl_3{\cdot}OR$, $SiCl_2(OR)_2$, and $SiCl(OR)_3$, but not $Si(OR)_4$, where R = Bu^t or CMe_2Et, from reactions involving silicon tetrachloride, pyridine, and tertiary alcohol, and this result has recently been confirmed by Gerrard and Woodhead (*J.*, 1951, 519). In addition, Miner *et al.* (*loc. cit.*) demonstrated that the tri-*tert.*-butoxychlorosilane $SiCl(OBu^t)_3$ can be converted into the mixed alkoxide $Si(OBu^t)_3{\cdot}OBu^n$. Thus the reactivity of the chlorine in $SiCl(OR)_3$ is beyond doubt and it appears that steric considerations prevent the introduction of the fourth tertiary alkoxide group. We have attempted to prepare silicon tertiary alkoxides by alcohol interchange involving tetraethoxysilane but without success. In our previous communication (*loc. cit.*) attention was drawn to the remarkable shielding effect of four tertiary alkoxide groups around the titanium or zirconium atom and it is possible that the small radius of the silicon atom precludes the formation of tetra-*tert.*-alkoxides of this element. The chief point of interest is whether the tetra-*tert.*-alkoxides of silicon will be more or less volatile than the titanium analogues. From the boiling points of $Si(OBu^s)_2(OBu^t)_2$ and $Si(OBu^s)_4$ (Woodhead, Thesis, London, 1950), it is deduced that $Si(OBu^t)_4$ should have a boiling point close to 60°/0·5 mm., since the boiling points of the corresponding titanium (65°/0·5 mm.) and zirconium compounds (63°/0·5 mm.) show that there is probably little variation through the series.

Interest now moves to the heaviest element of Group IV since the size and electropositive nature of the thorium atom may play a dominant part in determining the properties of thorium tetra-*tert.*-alkoxides.

The unusual volatility relationship in the Ti, Zr, and Hf series of tertiary alkoxides reported in this communication serves as a reminder that other examples are known of compounds having "anomalous" boiling points (*e.g.*, CCl_4 and $SiCl_4$; $InCl_3$ and $TlCl_3$) and that no convincing explanation has as yet been given for these phenomena.

EXPERIMENTAL

Materials.—Silicon, titanium, and zirconium tetrachlorides were commercial products and used without further purification. 1-Ethyl-1-methylpropanol was prepared from ethyl methyl ketone and ethylmagnesium bromide. 1 : 1 : 2-Trimethyl- and 1 : 1 : 2 : 2-tetramethyl-propanol were obtained from reactions involving acetone and the appropriate Grignard reagents. 1-Ethyl-1 : 2-dimethylpropanol was prepared from ethyl methyl ketone and *iso*propylmagnesium bromide. 1 : 1-Diethylpropanol was obtained from ethyl carbonate and ethylmagnesium bromide. Other alcohols used were the purest commercial products available. With the exception of *tert.*-butyl alcohol all the tertiary alcohols were azeotropically dried and carefully purified by fractionation through a column (70 cm.) packed with Fenske helices. *tert.*-Butyl alcohol was first dried with quicklime and then distilled over sodium. Pyridine ("AnalaR") was dried over barium oxide and distilled. The lower alcohols and solvents were dried and purified by the methods previously described (Bradley and Wardlaw, *J.*, 1951, 280; Bradley, Mehrotra, and Wardlaw, Part I, *loc. cit.*).

Analytical Methods.—Silicon, titanium, zirconium, methoxide, ethoxide, or *iso*propoxide were determined as previously described. In the mixed alkoxides ethoxide could be determined in the presence of *tert.*-butoxide without modification of the normal method, but for methoxide in the presence of *tert.*-butoxide an empirical method was used. Carbon and hydrogen analyses were by Messrs. Weiler and Strauss (Oxford) whom we thank for their co-operation.

Molecular Weights.—Molecular weights (see Table) were determined ebullioscopically in benzene (Bradley, Mehrotra, and Wardlaw, *loc. cit.*). One apparatus gave an ebullioscopic constant of 31·5 whereas a second gave 29·8. Determinations in the latter apparatus are marked by an asterisk.

Alkoxide	Range of *m* (g.)	No. of determns.	Benzene (c.c.)	$\Delta T/m$ (°/g.)	*M*, found	*M*, calc.
$Ti(O{\cdot}CMe_3)_4$ *	0·169—1·644	5	37·6	0·228	347 †	340·3
$Zr(O{\cdot}CMe_3)_4$ *	0·084—0·844	5	37·5	0·208	381	383·7
$Ti(O{\cdot}CMe_2Et)_4$	0·222—1·357	5	34·0	0·229	404	396·5
$Zr(O{\cdot}CMe_2Et)_4$	0·555—2·037	4	35·9	0·193	454	439·8
$Ti(O{\cdot}CMeEt_2)_4$	0·177—1·506	5	36·3	0·183	474	452·5
$Zr(O{\cdot}CMeEt_2)_4$	0·104—1·656	5	35·6	0·172	514	496
$Zr(O{\cdot}CEt_3)_4$	0·143—1·563	6	35·8	0·1655	532	552

† Cullinane *et al.* (*J. Appl. Chem.*, 1951, **1**, 400) found *M*, 315 (cryoscopic in benzene).

Boiling Points.—B. p.s at low pressures were measured in the apparatus described in Part I (*loc. cit.*). B. p.s over a range of pressures were determined in a special all-glass apparatus consisting of a flask (10 c.c.) joined through a semimicro-Claisen head to a total condensation variable take-off stillhead. Thus b. p.s under conditions of total reflux were measured and the purity of the alkoxide could be checked by collecting fractions. The rate of reflux, size of capillary leak, and temperature difference between heating-bath and thermometer pocket were standardised to be the same in each experiment. Pressures were read on a mercury manometer.

Preparation of Alkoxides.—Except for the *tert.*-butoxides the alkoxides were prepared by alcohol interchange involving the *iso*propoxide and the appropriate higher alcohol. Titanium tetra-*tert.*-butoxide was prepared from the tetrachloride by Cullinane, Chard, Price, and Millward's method (*J. Soc. Chem. Ind.*, 1950, **69**, S38). Although zirconium tetra-*tert.*-butoxide was obtained by Bradley and Wardlaw (*loc. cit.*) the yields were small and hence other methods were investigated. Alcohol interchange involving either the tetramethoxide or tetraethoxide of zirconium gave only mixed alkoxides but the tetra-*tert.*-butoxide was obtained by thermal disproportionation of the mixed alkoxide. The *iso*propoxides of titanium and zirconium were prepared by the methods described in Part I.

Titanium tetra-tert.*-butoxide.* Titanium tetrachloride (55 g.) was added dropwise with constant stirring to *tert.*-butyl alcohol (167 g.) and pyridine (55 g.) in benzene (150 c.c.). Ammonia was passed into the mixture until the products had cooled to room temperature. After filtration and evaporation of the filtrate the final product distilled as a colourless liquid (78 g.), b. p. 107—108°/10 mm. (Found: Ti, 14·0. Calc. for $C_{16}H_{36}O_4Ti$: Ti, 14·1%). B. p.s: 64·5°/0·4, 69·5°/0·8, 81°/2·0, 91°/4·2, 96°/5·7, 100°/7·0, 106°/9·0, and 109°/11·0 mm.

Zirconium tetra-tert.*-butoxide.* (*a*) Zirconium tetramethoxide was prepared by the action of methanol (106 g.) on zirconium *iso*propoxide (32·4 g.) in benzene (77 g.). After 4 hours' refluxing the gelatinous precipitate was filtered off and refluxed with more methanol (150 g.) for 6 hours. The solid product was dried for 2 hours at 160°/0·1 mm. (Found: Zr, 41·3. Calc. for $C_4H_{12}O_4Zr$: Zr, 42·4%). To the foregoing product (11·0 g.) was added *tert.*-butyl alcohol (120 g.) and benzene (500 c.c.); the mixture was boiled and volatile products were fractionated through a column (70 cm.) packed with Fenske helices. The white solid slowly dissolved and the b. p. of the distillate under total reflux fell to 59° (b. p. of methanol–benzene azeotrope). During 2 hours distillate (10 c.c.) boiling between 59° and 64° was collected, then the b. p. rose rapidly to 72°. Fractionation was continued at a high reflux ratio for 12 hours until pure benzene was collected. The clear solution (30 c.c.) deposited crystals (9·8 g.) (Found: Zr, 27·8%). The solid product was recrystallised from benzene (20 c.c.) and proved to be a mixed alkoxide (6·0 g.) [Found: Zr, 27·7; MeO, 11·1. Calc. for a mixture of $Zr(OBu)_3{\cdot}OMe$ (4 mols.) and $Zr(OMe)_2(OBu)_2$ (1 mol.): Zr, 27·4; MeO, 11·2%]. The mixed alkoxide (5·4 g.) was heated at 8 mm., melting at 60—70°, and boiling at 180° to give a distillate, b. p. 100°/8 mm. Heating was continued for 4 hours at 220°, after which volatile material was collected at 1 mm. The white residue (1·4 g.) showed no loss in weight after prolonged heating at 220° (Found: Zr, 35·1, MeO, 33·4%; MeO : Zr, 2·8) and appeared to be mainly zirconium mono-*tert.*-butoxide trimethoxide. The volatile product was redistilled and gave a colourless mobile liquid (2·6 g.), b. p. 86°/4 mm. (Found: Zr, 23·9. Calc. for $C_{16}H_{36}O_4Zr$: Zr, 23·8%). The disproportionation appears to take the course $3Zr(OBu^t)_3{\cdot}OMe \longrightarrow 2Zr(OBu^t)_4 + Zr(OMe)_3{\cdot}OBu^t$.

(*b*) To zirconium tetraethoxide [30 g.; prepared from $(C_5H_6N)_2ZrCl_6$ by the method of Bradley, Halim, Sadek, and Wardlaw, *J.*, 1952, 2023] were added *tert.*-butyl alcohol (54 g.) and benzene (400 c.c.), and the mixture was fractionally distilled (90-cm. column). During the first 2 hours benzene–ethanol azeotrope (29 g., 50%) was collected and thereafter subsequent interchange was very slow, the b. p. of distillate rising from 69° to 73°. Removal of solvent left a very viscous liquid (36·7 g.) which was caused to disproportionate at 180°/0·4 mm. for several hours until no more volatile product was collected. A very viscous residue remained

(27·9 g.) (Found: Zr, 28·0%). After some weeks this residue gave more volatile products when heated at a higher temperature (220°) and pressure (8·5 mm.). When disproportionation had ceased the viscous residue was itself distilled (16·1 g.; b. p. 195°/1·4 mm.) (Found: Zr, 29·0%). This compound suffered no further disproportionation when heated at 240°/8·5 mm. and was redistilled, giving a very viscous distillate (14·6 g.; b. p. 190°/1·5 mm.) (Found: Zr, 28·9; EtO, 25·0%; EtO : Zr, 1·75). This remarkably stable mixed alkoxide of zirconium is evidently mainly $Zr(OEt)_2(OBu^t)_2$. The combined volatile products (13·2 g.) were shown by distillation (b. p. 100·5°/8·5 mm.) to be zirconium tetra-*tert.*-butoxide.

B. p. of $Zr(OBu^t)_4$: 55°/0·2, 72°/1·1, 74·5°/1·5, 79·5°/2·5, 85·5°/4·0, 92·5°/6·0, 100·5°/8·5, 102°/10, and 104°/12 mm.

Titanium tetra-(1 : 1-*dimethylpropoxide*). Prepared as in Part I, this had b. p.s 109·5°/0·3, 114·5°/0·6, 126°/2·0, 138°/4·0, 150°/7·0, 154°/8·7, and 157·5°/10·0 mm.

Zirconium tetra-(1 : 1-*dimethylpropoxide*). Prepared as in Part I, this had b. p.s 93·0°/0·1, 123°/2·0, 134°/4·0, 144°/6·7, 145·5°/7·5, and 153°/10·0 mm.

Titanium tetra-(1-*ethyl*-1-*methylpropoxide*). Titanium *iso*propoxide (3·5 g.) in benzene (80 c.c.) was heated with 1-ethyl-1-methylpropanol (7·3 g.; b. p. 122°/760 mm.), and the benzene–propan-2-ol azeotrope collected by fractionation. After the removal of solvent the new *alkoxide* was distilled and gave a colourless liquid (5·0 g.), b. p. 154°/2 mm. (Found: Ti, 10·65; C, 64·1; H, 11·5. $C_{24}H_{52}O_4Ti$ requires Ti, 10·6; C, 63·7; H, 11·6%). B. p.s: 139°/0·8, 149°/1·5, 154°/2·0, 161°/3·3, 166°/4·0, 172°/5·6, 178·5°/7·5, 184°/9·8, and 187°/11·0 mm.

Zirconium tetra-(1-*ethyl*-1-*methylpropoxide*). From the reaction involving zirconium *iso*propoxide (7·5 g.) and 1-ethyl-1-methylpropanol (11·2 g.) in benzene (70 c.c.) the benzene–propan-2-ol azeotrope (24 c.c.) was collected. After removal of solvent the new *alkoxide* was twice distilled and gave a colourless mobile liquid (8·0 g.), b. p. 150°/1·2 mm. (Found: Zr, 18·7; C, 56·8; H, 11·2. $C_{24}H_{52}O_4Zr$ requires Zr, 18·4; C, 58·1; H, 10·6%). B. p.s: 150°/1·2, 154°/1·7, 161·5°/3·0, 171°/5·0, 178·5°/7·0, 180°/7·5, 186°/9·8, and 186·5°/10·0 mm.

Titanium tetra-(1 : 1-*dimethylbutoxide*). Titanium *iso*propoxide (9·2 g.) in benzene (70 c.c.) was caused to react with 1 : 1-dimethylbutanol (15 g.; b. p. 123°/757 mm.) and the benzene–propan-2-ol azeotrope removed by fractionation. Removal of solvent left the new *alkoxide* which on distillation gave a colourless mobile liquid (13·5 g.), b. p. 141°/0·8 mm. (Found: Ti, 10·5. $C_{24}H_{52}O_4Ti$ requires Ti, 10·6%). B. p.s: 141°/0·8, 146°/1·5, 154°/2·5, 162°/4·0, 165·5°/4·8, 174°/7·0, 175°/7·5, and 181°/10·5 mm.

Zirconium tetra-(1 : 1-*dimethylbutoxide*). The reaction between zirconium *iso*propoxide (8·4 g.) and 1 : 1-dimethylbutanol (10·0 g.) was carried out in benzene (70 c.c.) in the usual way. The new *alkoxide* was a yellow mobile liquid (8·0 g.), b. p. 133°/0·7 mm. (Found: Zr, 18·3. $C_{24}H_{52}O_4Zr$ requires Zr, 18·4%). B. p.s: 133°/0·7, 137°/1·0, 144°/1·7, 151°/2·8, 157°/4·0, 164°/5·6, 171°/8·0, and 176°/10·0 mm.

Titanium tetra-(1 : 1 : 2-*trimethylpropoxide*). From the reaction involving titanium *iso*propoxide (7·9 g.) and 1 : 1 : 2-trimethylpropanol (12·1 g.; b. p. 119°/740 mm.) in benzene (60 c.c.) the new *alkoxide* was obtained as a colourless mobile liquid (10·4 g.), b. p. 147°/0·5 mm., 153°/1·0 mm. (Found: Ti, 10·5. $C_{24}H_{52}O_4Ti$ requires Ti, 10·6%).

Zirconium tetra-(1 : 1 : 2-*trimethylpropoxide*). Zirconium *iso*propoxide (7·4 g.) in benzene (80 c.c.) was caused to react with 1 : 1 : 2-trimethylpropanol, and the new *alkoxide* was isolated in the usual manner. On distillation a residue remained and the distillate was a brown mobile liquid (5·6 g.). Redistillation gave, with slight decomposition, a pale yellow liquid (4·5 g.), b. p. 133°/0·1 mm. (Found: Zr, 17·2; C, 61·2; H, 10·7. Calc. for $C_{24}H_{52}O_4Zr$: Zr, 18·4; C, 58·1; H, 10·1%). The zirconium alkoxide was evidently contaminated by *ca.* 5% of an organic substance from which it could not be separated by distillation. Although the experiment was repeated with a newly synthesised sample of 1 : 1 : 2-trimethylpropanol similar results were obtained and the alkoxide boiled at 150°/1·0 mm.

Titanium tetra-(1 : 1 : 2 : 2-*tetramethylpropoxide*). The interchange involving titanium *iso*propoxide (4·3 g.) and 1 : 1 : 2 : 2-tetramethylpropanol (8·2 g.; b. p. 131°/757 mm.) in benzene (80 c.c.) required 6 hours for completion. The new *alkoxide* was obtained as a pale yellow very viscous distillate (5·4 g.), b. p. 163°/0·5 mm. (Found: Ti, 9·45. $C_{28}H_{60}O_4Ti$ requires Ti, 9·4%).

Zirconium tetra-(1 : 1 : 2 : 2-*tetramethylpropoxide*). The addition of 1 : 1 : 2 : 2-tetramethylpropanol (6·1 g.) to zirconium *iso*propoxide (4·7 g.) produced an instant yellow coloration. After the addition of benzene (80 c.c.) the reaction was carried out in the usual way but was so slow that only a few drops of azeotrope were obtained and most of the distillate boiled between 76° and 77°. The new zirconium *alkoxide* was distilled (163°/0·3 mm.) with difficulty, owing to its tendency to block the apparatus. Redistillation gave a yellow solid (b. p. 168°/0·5 mm.) (Found: Zr, 16·6; C, 58·6; H, 10·3. $C_{28}H_{60}O_4Zr$ requires Zr, 16·5; C, 60·9; H, 11·0%).

Titanium tetra-(1-*ethyl*-1 : 2-*dimethylpropoxide*). Titanium *iso*propoxide (3·0 g.) and 1-ethyl-1 : 2-dimethylpropanol (6·5 g.; b. p. 142°/765 mm.) were heated together at 150—160° in benzene (70 c.c.) for 4 hours before the interchange was complete. The new *alkoxide* was distilled (197°/1·0 mm.) and set to a very viscous colourless liquid (4·2 g.) (Found: Ti, 9·5; C, 66·3; H, 11·6. $C_{28}H_{60}O_4Ti$ requires Ti, 9·4; C, 66·1; H, 11·9%).

Zirconium tetra-(1-*ethyl*-1 : 2-*dimethylpropoxide*). The interchange involving 1-ethyl-1 : 2-dimethylpropanol (5·9 g.) and zirconium *iso*propoxide (4·0 g.) in benzene (90 c.c.) required 12 hours for completion. The new *alkoxide* was a mobile liquid (4·2 g.), b. p. 194°/0·7 mm. (Found: Zr, 16·5; C, 60·7; H, 10·8. $C_{28}H_{60}O_4Zr$ requires Zr, 16·5; C, 60·9; H, 11·0%).

Titanium tetra-(1 : 1-*diethylpropoxide*). From the reaction involving titanium *iso*propoxide (3·5 g.) and 1 : 1-diethylpropanol (7·5 g.; b. p. 142°/758 mm.) in benzene (80 c.c.) the new *alkoxide* was recovered in the usual way. The compound was distilled with difficulty (m. p. 140°; b. p. 180°/0·5 mm.) and the colourless distillate set to a glass (Found: Ti, 9·5; C, 66·2; H, 12·0. $C_{28}H_{60}O_4Ti$ requires Ti, 9·4; C, 66·1; H, 11·9%).

Zirconium tetra-(1 : 1-*diethylpropoxide*). Zirconium *iso*propoxide (8·7 g.) and 1 : 1-diethylpropanol (13·5 g.) were caused to react in benzene (80 c.c.), and the new *alkoxide* was isolated as before. The colourless product (10·3 g.) set to a glass after distillation (180°/0·4 mm.) (Found: Zr, 16·6; C, 59·7; H, 10·85. $C_{28}H_{60}O_4Zr$ requires Zr, 16·5; C, 60·9; H, 11·0%).

Reaction between Ethyl Orthosilicate and 1 : 1-*Dimethylpropanol*.—Ethyl orthosilicate (3·9 g.; prepared from ethanol and silicon tetrachloride) and 1 : 1-dimethylpropanol (9·1 g.) were heated together at 140—150° in benzene (60 c.c.) in the apparatus containing the fractionating column (70 cm.) Throughout 8 hours the b. p. under total reflux remained constant at that of pure benzene, showing that no interchange had occurred. On addition of zirconium tetra-1 : 1-dimethylpropoxide (1·0 g.) as a catalyst the b. p. fell to 70° in 20 minutes. Removal of distillate (6·0 c.c.; b. p. 72—73°) caused a rise in b. p. and fractionation was continued at a high reflux ratio until pure benzene was collected. After removal of solvent the liquid mixed alkoxide was distilled under atmospheric pressure and gave a main fraction boiling at 180—185° [Found: Si, 10·5; Zr, <0·2. Calc. for $Si(OEt)_3{\cdot}OC_5H_{11}$: Si, 11·2%]. The residual liquid distilled at 210°/200 mm. (Found: Zr, 12·3; Si, 4·1%).

Fractional Distillation of Zirconium Tetra-(1 : 1-*dimethylpropoxide*).—Zirconium tetra-1 : 1-dimethylpropoxide (25 g.; containing HfO_2, 2·1% based on the mixed oxides) was fractionated at 160—180° through a column (45 cm.) packed with Fenske helices. The distillate (1 c.c.; b. p. 100°/0·3 mm.) was collected at a 10 : 1 reflux ratio (Found: Hf, 3·2 ± 0·2%). The experiment was terminated because of leakage, the remaining alkoxide containing 2·1 ± 0·2% of hafnium.

A second sample (47·5 g.; Hf, 0·8 ± 0·1%) was fractionated in the same apparatus at the reflux ratio 10 : 1. The first fraction (7·5 g.; b. p. 100°/0·3 mm.; Hf, 1·2 ± 0·1%) was again enriched in hafnium. Flooding and decomposition then interfered with fractionation and the combined second and third fractions (25 g.) had the same hafnium content (0·8 ± 0·1%) as the initial material. The remaining undistilled alkoxide had a slightly lower hafnium content (0·7 ± 0·1%). It is hoped that with an improved design of apparatus it will be possible to separate hafnium from zirconium by this method.

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