979. *Structural Chemistry of the Alkoxides. Part III.* Secondary Alkoxides of Silicon, Titanium, and Zirconium.*

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The secondary alkoxides, $M(O{\cdot}CHR_2)_4$ where R = Me, Et, Pr^n, Pr^i, or Bu^n, and $M(O{\cdot}CHMeR)_4$ where R = Et, Pr^n, Pr^i, Bu^n, Bu^t, or *n*-hexyl, and M = Ti or Zr, have been prepared, and also *iso*propyl and *sec.*-amyl orthosilicates. Boiling points and, in some cases, vapour pressures and molecular weights have been measured. The results support the theory that steric effects are most important in determining the physical properties of the alkoxides. Entropies of vaporisation for $Si(OPr^i)_4$, $Si(O{\cdot}CHEt_2)_4$, $Ti(OPr^i)_4$, and $Ti(O{\cdot}CHEt_2)_4$ exhibit some anomalous relations which are discussed.

Bradley, Mehrotra, and Wardlaw (*J.*, 1952, 2027, 4204) suggested that steric effects play an important part in determining the structure and volatility of alkoxides of silicon, titanium, and zirconium. It was predicted that the powerful shielding of the central atom by branched alkoxide groups would prevent strong intermolecular bonding by tertiary alkoxides of titanium or zirconium and these were actually found to be monomeric. However, the alternative explanation was also considered that the strong ($+I$) inductive effect of the tertiary alkyl group could be responsible for the striking properties of the tertiary alkoxides.

In an endeavour to resolve these possibilities a detailed study of the secondary alkoxides has been made. The following series of compounds were prepared: $M(O{\cdot}CHR_2)_4$ where R = Me, Et, Pr^n, Pr^i, or Bu^n; and $M(O{\cdot}CHMeR)_4$ where R = Et, Pr^n, Pr^i, Bu^n, Bu^t, or *n*-hexyl. In the first series, the derivatives of the symmetrical dialkylcarbinols, the steric effect will increase rapidly with size of the alkyl group but the $+I$ effect will soon reach saturation. In the other series more gradual steric effects can be achieved. The new alkoxides were prepared by alcohol interchange from the *iso*propoxides. Molecular weights and boiling points were measured by methods previously described (*locc. cit.*). The results are collected in Table 1 (X = molecular complexity = M/Formula weight).

The contrast between titanium and zirconium is clearly shown. For example, in the

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* Part II, *J.*, 1952, 4204.

TABLE 1.

	Ti alkoxide			Zr alkoxide		
Alkyl	B. p. (0·1 mm.)	*M*	*X*	B. p. (0·1 mm.)	*M*	*X*
$Me_2CH\cdot$	49°	390	1·4	160°	967	3·0
$Et_2CH\cdot$	112	399	1·0	181	868	2·0
$Pr^n_2CH\cdot$	156	500	1·0	163	545	1·0
$Pr^i_2CH\cdot$	162	474	1·0	158	557	1·0
$Bu^n_2CH\cdot$	195	—	—	198	—	—
MeEtCH·	81	—	—	164	909	2·5
$MePr^nCH\cdot$	115	410	1·0	178	860	2·0
$MePr^iCH\cdot$	117	415	1·0	176	870	2·0
$MeBu^nCH\cdot$	126	—	—	190	—	—
$MeBu^tCH\cdot$	127	—	—	128	481	1·0
$Me(C_6H_{13})CH\cdot$	182	—	—	212	1039	1·7

dialkylcarbinol series the titanium derivatives, with the exception of the lowest member, are monomeric whereas in the zirconium series the molecular complexity changes from 3 to 2 to 1 as the alkyl groups are changed from methyl to ethyl to propyl. It is noteworthy that the monomeric secondary alkoxides of zirconium are close in volatility to their titanium analogues as would be expected for monomeric alkoxides (cf. Part II, *loc. cit.*). In the alkylmethylcarbinol series the titanium derivatives are monomeric when R in $Ti(O\cdot CHMeR)_4$ is propyl or higher whilst the molecular complexity of the zirconium derivatives decreases from 3 to 2 to 1·7 as the alkyl chain is increased from methyl to ethyl to *n*-hexyl. This behaviour emphasises the steric nature of the effects being investigated since in the zirconium series none of the 1-methylalkyloxides shows as complete shielding as the derivatives of the dipropylcarbinols. Moreover, the introduction of more remote branching in the alkylmethylcarbinol series considerably enhances the shielding. Thus, the zirconium derivative of *n*-butylmethylcarbinol is complex (X between 1·7 and 2·0) and has a much higher boiling point than the monomeric zirconium derivative of the isomeric *tert.*-butylmethylcarbinol. A similar contrast in properties was found between the zirconium derivatives of the *n*-butyl- and *tert.*-butyl-carbinol (Part I, *loc. cit.*). The evidence so far presented strongly favours the suggestion that it is the steric effect of the alkoxide group and not the $+I$ effect of the alkyl group which is responsible for the remarkable properties of zirconium alkoxides.

This view is supported by the data in Table 2, which show that the boiling points of isomeric monomeric alkoxides of titanium and zirconium are close together irrespective of whether the alkoxide is secondary or tertiary. In view of the greater shielding requirements of the zirconium atom it is not expected that monomeric zirconium normal alkoxides will be found although titanium normal alkoxides with long chains may be monomeric.

TABLE 2.

	Ti alkoxide			Zr alkoxide	
Alkyl	B. p. (0·1 mm.)	B. p. (0·1 mm.)	Alkyl	B. p. (0·1 mm.)	B. p. (0·1 mm.)
Bu^tMeCH	127°	128°	Pr^i_2CH	162°	158°
Et_2MeC	122	127	Et_3C	166	168
Pr^n_2CH	156	163	Bu^tMe_2C	149	154

Only a few secondary alkoxides of silicon have hitherto been prepared (*viz.*, *sec.*-butyl Ridge and Todd, *J.*, 1949, 2637, and *sec.*-octyl, Gerrard and Woodhead, *J.*, 1951, 519). Dearing and Reid (*J. Amer. Chem. Soc.*, 1928, **50**, 3058) were unable to obtain *iso*propyl orthosilicate from the reaction involving silicon tetrachloride and *iso*propyl alcohol, but we obtained a good yield from these reagents. Similarly the reaction between diethylcarbinol and silicon tetrachloride afforded the required alkoxide. Boiling points were measured at various pressures for the new silicon alkoxides, the first three members of the series of titanium secondary alkoxides, and zirconium *iso*propoxide. In the pressure range 2·0—10·0 mm. Hg the data conformed to the characteristic equation : $\log p_{\text{mm.}} = a - b/T$. The values of a, b, boiling point at 5·0 mm. ($T_{5\cdot0}$), latent heat of vaporisation (L_V, kcal. mole^{-1}), and the entropy of vaporisation at 5·0 mm. ($\Delta S_{5\cdot0}$, cal. mole^{-1} deg.$^{-1}$) are presented in Table 3.

The normal boiling points of the *iso*propoxides of silicon and titanium were also measured and were respectively 186° and 220°, giving the corresponding Trouton constants 24·4 and 29·9. The high Trouton constant for *iso*propyl orthosilicate is interesting in view of the monomeric nature of this substance and suggests that strong intermolecular forces are present. The higher entropy of vaporisation of titanium *iso*propoxide than its silicon analogue is not surprising since the former compound shows a molecular complexity of 1·4 in boiling benzene. The remarkably high entropy of vaporisation of zirconium *iso*propoxide is of great theoretical interest and will be discussed in detail in Part IV. However, it is noteworthy that the increase in molecular complexity (in solution) of the tetra*iso*propoxides as the central atom is changed from silicon ($X = 1{\cdot}0$) to titanium ($X = 1{\cdot}4$) to zirconium ($X = 3{\cdot}0$) is reflected in the parallel increase in entropy of vaporisation $\Delta S_{5\cdot0}$.

According to our present theory we should expect monomeric tetra-alkoxides of silicon, titanium, and zirconium to have approximately the same entropies (cf. tertiary alkoxides of titanium and zirconium, Part II, *loc. cit.*). Table 3 shows that for certain monomeric secondary alkoxides this is not the case. For example, although *iso*propyl and *sec.*-amyl orthosilicate are undoubtedly monomeric they differ by 6·9 units in entropy of vaporisation and the compound which has the more shielded central atom has, unexpectedly, the higher entropy of vaporisation. In addition the monomeric titanium derivative of diethylcarbinol has an entropy of vaporisation 8·7 units greater than that of its silicon analogue. Whilst the latent heat values are considered as provisional, pending precision vapour-pressure measurements, it is believed that the anomalous differences in entropy of vaporisation quoted above are outside the limits of experimental error. Hitherto attention has been focused on intermolecular attraction involving oxygen and the central atom M in $M(OR)_4$ but these new anomalies suggest that strong intermolecular attraction of another kind involving the alkyl groups is also present. Two mechanisms seem reasonable to explain the abnormally greater structure in the liquid than in the vapour as the size of the alkyl group is increased. The first mechanism involves "entanglement" of neighbouring alkyl groups in the liquid state, thus providing an additional entropy requirement in the vaporisation process, whilst an alternative explanation lies in the possibility that rotation of the alkoxy-groups is more restricted in the liquid than in the vapour. It is clear that alkyl-group interaction would be expected to feature decisively in the properties of the straight-chain normal alkoxides which will be dealt with in Part IV.

TABLE 3.

Alkoxide	$T_{5\cdot0}$	a	b	L_v	$\Delta S_{5\cdot0}$	Alkoxide	$T_{5\cdot0}$	a	b	L_v	$\Delta S_{5\cdot0}$
$Si(OPr^i)_4$	55·8°	8·1	2440	11·2	34·0	$Ti(O{\cdot}CHMeEt)_4$	127·8°	11·9	4345	19·9	49·6
$Si(O{\cdot}CHEt_2)_4$	139·0	9·7	3690	16·9	40·9	$Ti(O{\cdot}CHEt_2)_4$	157·3	11·6	4640	21·4	49·6
$Ti(OPr^i)_4$	91·3	9·6	3225	14·7	40·5	$Zr(OPr^i)_4$	203·8	15·16	6895	31·5	66·1

EXPERIMENTAL

All-glass apparatus was used and special precautions were taken to exclude moisture. The methods for analysing the alkoxides and for drying and purifying solvents have previously been described (Bradley, Mehrotra, and Wardlaw, Parts I and II, *locc. cit.*). The alcohols used were of the purest grade commercially available except for 1-methylbutanol, 1 : 2-dimethylpropanol, and 1-*n*-butylpentanol which were synthesised by the usual methods involving Grignard reagents. All the alcohols were finally purified by fractionation with a column (70-cm.) packed with Fenske helices. The same column was used in the alcohol-interchange experiments. The methods for determining molecular weights and boiling points and for preparing the alkoxides have previously been described (*loc. cit.*).

iso*Propyl Orthosilicate*.—Silicon tetrachloride (18 g.) was added slowly to *iso*propyl alcohol (39·4 g.) at 0°. A vigorous reaction occurred with evolution of hydrogen chloride. Dry nitrogen was passed through the liquid for 2 hr. to remove hydrogen chloride and complete the reaction. The excess of *iso*propyl alcohol and remaining hydrogen chloride were removed by evaporation under reduced pressure for 12 hr. at room temperature. The final *product* was distilled (b. p. 74°/13 mm.) and gave a colourless mobile liquid (16·6 g.), b. p. 44°/2·5, 52°/4·0, 61°/6·5, 62°/7·0, 66°/8·7, 70°/10·0, 74°/13, 116°/85, 152°/400, 185°/753 mm. [Found : Si, 10·6. $Si(OC_3H_7)_4$ requires Si, 10·6%].

Titanium iso*Propoxide*.—The compound, prepared as described by Bradley, Mehrotra, and Wardlaw (*J.*, 1952, 2027), had b. p. 61°/0·4, 69°/1·0, 72°/1·5, 77°/2·0, 82°/3·0, 89°/4·5, 92°/5·0, 95·5°/6·5, 97°/7·0, 100°/8·2, 102°/9·1, 104°/10·0, 132°/41, 154°/100, 189°/310, 220°/760 mm.

Zirconium iso*Propoxide*.—The complex *iso*propoxide was prepared as described by Bradley, Mehrotra, and Wardlaw (*J.*, 1952, 2027) and converted into the tetra*iso*propoxide by heating it at 100° under reduced pressure. The vapour-pressure determinations are probably less accurate than for the other compounds owing to the high b. p. The compound had b. p. 190·6°/2·0, 195·3°/2·7, 199°/3·5, 202°/4·0, 206·5°/6·5, 208°/7·1, 211·5°/8·0, 212°/9·0 mm.

Titanium Tetra-(sec.*-butoxide*).—Titanium *iso*propoxide (25·0 g.) was caused to react with 1-methylpropanol (b. p. 99°/750 mm.; 49·0 g.) in benzene (120 c.c.), and the benzene-*iso*-propanol azeotrope removed by fractionation. After evaporation of the solvent the product was distilled and gave a colourless mobile liquid (24·1 g.), b. p. 105°/1·2, 111°/1·9, 120°/3·2, 124°/4·0, 128°/5·0, 132°/6·3, 136·5°/8·0, 139°/9·0, 141°/10·0 mm. [Found: Ti, 14·1. Calc. for $Ti(OC_4H_9)_4$: Ti, 14·1%].

Other *alkoxides*, similarly prepared, are recorded in Table 4.

1-*Ethylpropyl Orthosilicate*.—Silicon tetrachloride (10·0 g.) was added dropwise to 1-ethylpropanol (b. p. 116°/760 mm.; 22·4 g.) at *ca.* −78° and a brisk evolution of hydrogen chloride occurred. The liquid product was allowed to attain room temperature and dry nitrogen was then aspirated through it for 2 hr. Excess of alcohol and hydrogen chloride were removed at 10 mm. and the remaining liquid was distilled (b. p. 100—110°/0·5 mm.). The distillate (19·4 g.), which still contained chloride, was refluxed with 1-ethylpropanol (8 g.) for 2 hr. and then hydrogen chloride removed in nitrogen. After removal of excess of alcohol the new alkoxide (12·5 g.) was distilled (b. p. 102°/0·5 mm., 91°/0·1 mm.) [Found: Si, 7·6. $Si(OC_5H_{11})_4$ requires Si, 7·45%]. B. p.s were 98°/0·3, 110°/1·0, 119°/1·7, 122°/2·0, 127°/2·6, 131°/3·4, 135°/4·1, 137°/4·6, 140·5°/5·6, 142°/6·0, 145°/7·0, 148°/8·0, 150°/8·8, 152°/9·5, 153·5°/10·0 mm.

TABLE 4. *Preparation and properties of titanium and zirconium alkoxides*, $M(OR)_4$.

R	$M(OPr^i)$ taken (g.)	ROH taken (g.)	C_6H_6 (c.c.)	Yield (g.)	B. p./mm.	Found: M, %	Reqd.: M, %
			Titanium compounds.				
$CHMeBu^n$	10·8	22·2	100	16·5 [a]	140°/0·5, 126°/0·1	10·6	10·6
$CHMeBu^t$	9·8	17·1	80	14·3	127°/0·1 [b]	10·6	10·6
$CHPr^n_2$	6·9	14·1	60	11·3	170°/0·5, 156°/0·1	9·5	9·4
$CHPr^i_2$	7·6	24·1	80	11·9 [c]	162°/0·1	9·5	9·4
$CHMe{\cdot}C_6H_{13}\text{-}n$	8·8	22·9	70	9·2	188°/0·2, 182°/0·1	8·5	8·5
$CHBu^n_2$	6·1	14·5	60	12·5	195°/0·1	7·7	7·7
			Zirconium compounds.				
CHMeEt	6·5	8·6	60	5·8	164°/0·1 [d]	23·8	23·8
$CHMeBu^n$	11·0	18·1	90	12·5	184°/0·05, 190°/0·1	18·5	18·4
$CHMeBu^t$	9·3	17·1	80	10·3	128°/0·1 [e]	18·5	18·5
$CHPr^n_2$	6·0	8·8	75	7·1	183°/1·0,[f] 163°/0·1	16·5	16·5
$CHPr^i_2$	5·5	14·4	80	7·3 [g]	158°/0·1	16·8	16·5
$CHMe{\cdot}C_6H_{13}\text{-}n$	7·5	11·3	80	6·3	224°/0·3 [h]	15·05	15·0
$CHBu^n_2$	6·8	11·6	70	11·2	198°/0·1 [d]	13·8	13·7

[a] 3 Hours for complete reaction. [b] Slowly crystallises. [c] 4 Hours for complete reaction. [d] Slowly solidifies to a glass. [e] Slowly crystallises; solidifies at −78°. [f] M. p. *ca.* 160°. [g] 7 Hours for complete reaction. [h] With decomp.

sec.-*Amyloxides of Titanium and Zirconium*.—For the preparation and the measurement of molecular weights see Part I (*loc. cit.*). The following b. p.s were recorded for titanium tetra-(1-ethylpropoxide): 112°/0·1, 119°/0·3, 126°/0·7, 134°/1·5, 142°/2·0, 151°/3·7, 160·5°/6·0, 166°/8·1, 172°/10·5 mm.

Ebullioscopic Results.—

Alkoxide	Range of wts. (g.)	Benzene, c.c.	*M*, found	*M*, calc.
$Ti(OPr^i)_4$	0·117—1·213	37·05	390	284·3
$Zr(OPr^i)_4$	0·218—2·089	36·2	967	327·5
$Zr(O{\cdot}CHMeEt)_4$	0·124—1·495	36·5	909	383·7
$Ti(O{\cdot}CHPr^n_2)_4$	0·105—1·280	36·0	500	508·7
$Zr(O{\cdot}CHPr^n_2)_4$	0·080—1·390	35·9	545	552·0
$Ti(O{\cdot}CHPr^i_2)_4$	0·205—1·917	35·0	474	508·7
$Zr(O{\cdot}CHPr^i_2)_4$	0·165—1·488	35·7	557	552·0
$Zr(O{\cdot}CHMeBu^t)_4$	0·173—1·161	35·3	481	495·9
$Zr(O{\cdot}CHMe{\cdot}C_6H_{13}\text{-}n)_4$	0·335—1·603	36·3	1039	608·1

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