412. *Structural Chemistry of the Alkoxides. Part IV.* Normal Alkoxides of Silicon, Titanium, and Zirconium.*

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The normal alkoxides, $Ti(OC_nH_{2n+1})_4$ where $n = 2, 3, 4, 5, 6, 7$, and 8, and $Zr(OC_nH_{2n+1})_4$ where $n = 2, 3, 4, 5, 6$, and 8, have been prepared and their molecular weights and boiling points measured. Molecular complexity is practically independent of chain length while boiling points increase linearly with molecular weight. Structures for the complex alkoxides are discussed. Vapour pressures and vapour densities were measured for zirconium tetraethoxide and tetra*iso*propoxide and it is suggested that the vaporisation process is $[Zr(OR)_4]_n$ (liquid) $\longrightarrow$ $nZr(OR)_4$ (vapour), and that the energy of intermolecular attraction is *ca.* 18 kcals./mole. Entropies of vaporisation for the *n*-alkoxides of silicon and titanium increase with chain length, and this behaviour is discussed in terms of molecular " entanglement " in the liquid state.

It has been established (Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 2027, 4204, 5020 *) that the structure and volatility of the alkoxides of titanium and zirconium are governed by the configuration of the alkyl group. The purpose of the present research was to study the effect of chain length on the molecular complexity and volatility of the *n*-alkoxides and to discover the nature and strength of intermolecular forces in the complex molecules. In addition, it was expected that more information concerning the alkyl-group interaction postulated in Part III * would be forthcoming from the study of the *n*-alkoxides of silicon, titanium, and zirconium.

The following *n*-alkoxides of titanium and zirconium were prepared: $Ti(OC_nH_{2n+1})_4$

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* Part III, *J.*, 1952, 5020.

where $n = 2, 3, 4, 5, 6, 7$, or 8, and $Zr(OC_nH_{2n+1})_4$ where $n = 2, 3, 4, 5, 6$, or 8. Except for the ethoxides these were prepared by alcohol interchange from the *iso*propoxides. Titanium tetraethoxide was prepared from the tetrachloride by the ammonia method (*loc. cit.*, p. 2027), and zirconium ethoxide was prepared by the method of Bradley, Halim, Sadek, and Wardlaw (*J.*, 1952, 2032) from pyridinium zirconium hexachloride. Zirconium *n*-hexyloxide could not be distilled without decomposition at 0·05 mm. and no attempt was made to distil zirconium *n*-octyloxide. Molecular weights (*M*) were determined on freshly distilled alkoxides in boiling benzene and the results, including molecular complexity (*X*) and boiling points, are presented in Table 1. This shows two outstanding features : (*a*) that molecular complexity in the zirconium alkoxides is much greater than in the titanium alkoxides and (*b*) that molecular complexity in both series is little affected by chain length. Whilst this work was in progress the results of Cullinane, Chard, Price, Millward, and Langlois (*J. Appl. Chem.*, 1951, **1**, 400) were reported. They found cryoscopically that molecular weights of titanium *n*-alkoxides (ethyl to *n*-hexyl) were approximately dimeric in benzene but that they depended on the concentration. Caughlan, Smith, Katz, Hodgson, and Crowe (*J. Amer. Chem. Soc.*, 1951, **73**, 5652), using the same method to determine the molecular weights of titanium tetraethoxide, tetra-*n*-propoxide, and tetra-*n*-butoxide, similarly found them to depend on concentration and to approach the trimeric state at high concentrations. It is interesting that our measurements in boiling benzene showed no significant variation of molecular weight of the titanium or zirconium compounds with concentration and that the molecular weight (in the titanium series) determined ebullioscopically is lower than that found cryoscopically. It appears that the molecular complexity of titanium *n*-alkoxides is a function of temperature. Neither titanium methoxide nor zirconium methoxide is soluble in suitable organic solvents and it was not possible to determine their molecular weights but this fact in conjunction with their very low volatilities suggests that they have complex structures.

TABLE 1.

	Titanium alkoxide			Zirconium alkoxide		
Alcohol	B. p./0·1 mm.	*M*	*X*	B. p./0·1 mm.	*M*	*X*
Ethanol	103°	556	2·4	180° *	980	3·6
Propanol	124	—	—	208	—	—
Butan-1-ol	142	—	—	243	1290	3·4
Pentan-1-ol	158	565	1·4	276	1428	3·2
Hexan-1-ol	176	—	—	>300	—	—
Heptan-1-ol	201	—	—	—	—	—
Octan-1-ol	214	781	1·4	—	2046	3·4

* Sublimed.

That molecular complexity is greater in zirconium alkoxides than in the corresponding titanium alkoxides can be explained as due either to stereochemical effects or to a difference in strength of the intermolecular binding. The stereochemical argument is very feasible in view of the greater atomic radius and maximum covalency of zirconium and evidence will be presented which suggests that the strength of intermolecular binding involving titanium and oxygen is comparable with that involving zirconium and oxygen.

Caughlan *et al.* (*loc. cit.*) suggested that each titanium atom in the trimeric alkoxides is surrounded octahedrally by oxygen atoms from alkoxide groups and that the trimeric unit comprises three octahedra bound by common faces. A similar arrangement seems reasonable for trimeric zirconium alkoxides but the molecular complexity in zirconium normal alkoxides is significantly greater than three. The fractional value suggests that a species of higher molecular complexity is present and a possible structure for a pentameric complex is shown in Fig. 1 in which octahedra share edges or faces. These structures involve zirconium with the co-ordination number 6 and the possibility that zirconium attains the co-ordination number 8 in these compounds cannot be ignored. However, the higher co-ordination number would lead to structures with a complexity much greater than three. Additional information concerning the nature of intermolecular bonding in the complex molecules has been obtained from molecular-weight determinations on zirconium ethoxide and zirconium *iso*propoxide in ethyl and *iso*propyl alcohol respectively. Thus zirconium ethoxide, which has a complexity of 3·6 in benzene, has a value of 2·5 in ethyl alcohol, whilst zirconium *iso*propoxide is trimeric in benzene and dimeric in *iso*propyl alcohol. The complexity of the zirconium alkoxide is lower in the alcohol presumably because bonds of type ${}^{R}_{H}{>}O{\rightarrow}Zr$ replace those of type ${}^{R}_{Zr}{>}O{\rightarrow}Zr$. The dimeric *iso*propoxide may well have the structure shown in Fig. 2. This structure has the empirical formula $Zr(OPr^i)_4,Pr^iOH$ which was found for the crystalline complex *iso*propoxide.

FIG. 1.

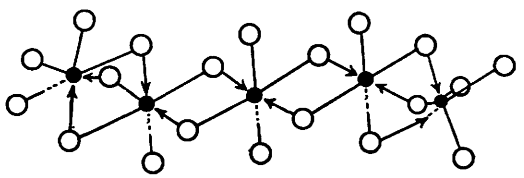
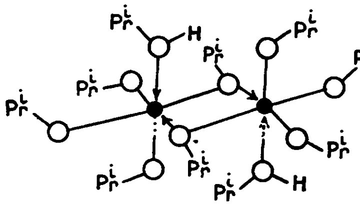


FIG. 2.



R *groups omitted.* $[Zr(OR)_4]_5$. ● = Zr; ○ = *Oxygen.*

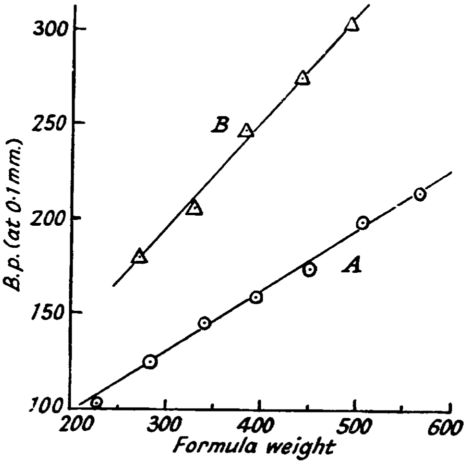


FIG. 3. *Normal alkoxides of* (A) *titanium, and* (B) *zirconium.*

The boiling points of the *n*-alkoxides of titanium and zirconium have been plotted against formula weights and the results are shown in Fig. 3. In both series there is a linear relation between boiling point and formula weight.

In Part I a linear relation between boiling point and molecular complexity was found for zirconium amyloxides and the possibility was envisaged that structure in the complex molecules might persist in the vapour state. Some preliminary vapour-pressure measurements have been made on zirconium tetraethoxide and tetra*iso*propoxide, and the results have given important information concerning the vaporisation process in these cases. The results conformed to the equation $\log p = a - b/T$ in the pressure range 2—10 mm. (see Table 2 where the symbols have their usual meaning; *loc. cit.*, p. 4204).

TABLE 2.

Alkoxide	$T_{5\cdot0}$	a	b	L_V	$\Delta S_{5\cdot0}$
$Zr(OEt)_4$	234·8	13·7	6600	30·2	59·4
$Zr(OPr^i)_4$	203·8	15·2	6895	31·5	66·0
$Zr(OBu^t)_4$	89·1	9·9	3330	15·2	42·0

Results for zirconium tetra-*tert.*-butoxide are given for comparison. The important factor which emerges is that the latent heats (L_V) and entropies of vaporisation (ΔS) are much greater for the complex alkoxides than for the monomeric zirconium *tert.*-butoxide. The abnormally high entropies of vaporisation suggest that the vaporisation process involves a change from a liquid containing complex molecules to a monomeric vapour state, *viz.* :

$$\underset{\text{Liquid}}{[Zr(OR)_4]_n} \rightleftharpoons \underset{\text{Vapour}}{nZr(OR)_4}$$

That the alkoxides are monomeric in the vapour state has been confirmed by vapour-density determinations on zirconium ethoxide and *iso*propoxide. These facts have enabled us to make a preliminary assessment of the energy of intermolecular bonding in the complex molecules. From the approximately linear relation between boiling point and formula weight in the monomeric *tert.*-alkoxides (*loc. cit.*, p. 4204) the boiling points ($T_{\text{mon.}}$) of zirconium ethoxide and *iso*propoxide in the hypothetical " monomeric " state have been calculated.

The hypothetical " monomeric " latent heats ($L_{\text{mon.}}$) were then obtained by assuming that entropies of vaporisation in the " monomeric " state are the same as for zirconium *tert.*-butoxide. Thus, $L_{\text{mon.}} = T_{\text{mon.}}\Delta S = 42{\cdot}0T_{\text{mon.}}$. The " monomeric " latent heats are $Zr(OEt)_4$ 12·6, and $Zr(OPr^i)_4$ 13·8 kcal./mole; and these values seem reasonable compared with the experimental value 15·2 kcal./mole for zirconium *tert.*-butoxide. The energy of intermolecular bonding in the complex alkoxides is then given by $E = L_v - L_{\text{mon.}}$; and the values for E are $Zr(OEt)_4$ 17·6, and $Zr(OPr^i)_4$ 17·7 kcal./mole. If it is further assumed that each zirconium atom participates in two intermolecular bonds with oxygen in the liquid state, then the energy of the $\overset{\text{Zr}}{\underset{\text{R}}{}}\!\!>\!O\!\rightarrow\!Zr$ bond is approximately 9 kcal. This is a relatively small value and suggests that the type of bonding may be electrostatic, $\overset{\delta+}{Zr}\cdots\overset{\delta-}{O}$, in nature rather than of the covalent type $\overset{-}{Zr}\text{–}\overset{+}{O}$. Brown, Taylor, and Sugishi's measurements (*J. Amer. Chem. Soc.*, 1951, **73**, 2464) of the dissociation of the addition compounds of trimethylboron with aliphatic amines gave values of the order of 18 kcal. for the energy of the boron–nitrogen bond which is probably of the covalent type, whereas the hydrogen bond which is believed to be electrostatic has a bond energy of the order of 4·5 kcal. (Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1940).

In Part III it was suggested that the anomalous entropies of vaporisation of certain monomeric alkoxides of silicon and titanium were due to interaction of the alkyl groups and that this conception could be tested by studying the *n*-alkoxides of silicon and titanium. Cullinane *et al.* (*loc. cit.*) gave boiling points at various pressures for the titanium *n*-alkoxides $Ti(OC_nH_{2n+1})_4$ where $n = 2$, 3, 4, 5, and 6. Although their data do not conform very accurately to the relation $\log p = a - b/T$, we have made provisional calculations of latent heats and entropies of vaporisation from them. In addition the vapour pressures of *n*-butyl and *n*-hexyl orthosilicate have been measured whilst the data for the ethyl orthosilicate have been taken from Post (" Organic Silicon Compounds," Reinhold Publ. Corp., New York, 1949). The latent heats and Trouton constants (Table 3) present strong evidence that alkyl-group interaction occurs in the *n*-alkoxides of silicon and titanium. In the case of ethyl orthosilicate the intermolecular attraction involving silicon and oxygen must be relatively small and should decrease steadily with increase in size of alkyl group. However, it is found that the entropies of vaporisation increase with alkyl chain length. This effect is partly due to the increase in Trouton's constant with decrease in vapour concentration at 760 mm. at the higher boiling points (cf. Hildebrand, *J. Amer. Chem. Soc.*, 1915, **37**, 970). Accordingly, the entropies of vaporisation (cal./deg./mole), corrected to the same vapour concentration, were calculated and found to be $Si(OEt)_4$ 25·7, $Si(OBu^n)_4$ 27·1 and $Si(OC_6H_{13\text{-}n})_4$ 31·7. We suggest that this increase

TABLE 3.

Alkoxide	L_V	Trouton constant	Alkoxide	L_V	Trouton constant
$Si(OEt)_4$	11·25	25·7	$Ti(OEt)_4$	21·6	42·5
$Si(OBu^n)_4$	14·84	28·0	$Ti(OPr^n)_4$	15·7	29·1
$Si(OHex^n)_4$	21·78	33·5	$Ti(OBu^n)_4$	20·1	35·6
			$Ti(OAm^n)_4$	23·1	39·4
			$Ti(OHex^n)_4$	24·6	40·5

in entropy of vaporisation with increase in chain length is due to molecular "entanglement" in the liquid state. A molecule $M(OC_nH_{2n+1})_4$ can be considered as equivalent to two chains of $(2n + 3)$ atoms fused at the central atom M and the possibility of entanglement of such tenuous structures is evident. A molecule in the liquid will require special orientation in order to be disentangled before vaporisation, and this increases the entropy of vaporisation. This theory enables us to interpret the surprising order of Trouton constants for the titanium normal alkoxides (Table 3). First, the high value for the ethoxide is attributed to the presence of complex molecules involving $^{\text{Ti}}_{\text{R}}{>}\text{O}\rightarrow\text{Ti}$ bonds and it is clear that the vaporisation process in $Ti(OEt)_4$ resembles that of the complex zirconium alkoxides. Thus $\Delta S_{5\cdot0}$ is 52·6 cal./deg./mole for $Ti(OEt)_4$ [cf. 59·4 for $Zr(OEt)_4$] and E is 10 kcal./mole [cf. 17·6 for $Zr(OEt)_4$]. If allowance is made for the greater shielding of titanium in $Ti(OEt)_4$ (complexity = 2·4) than of zirconium in $Zr(OEt)_4$ (complexity = 3·6) it seems possible that the energy of $^{\text{M}}_{\text{R}}{>}\text{O}\rightarrow\text{M}$ bonds is approximately the same for M = Ti or Zr. The greater shielding power of propoxide groups explains the decrease in molecular complexity and Trouton constant in passing from the ethoxide to the *n*- or *iso*-propoxide of titanium. Further increase in length of alkyl group leads to an increase in Trouton's constant, which can be ascribed to the predominance of the "entanglement" process.

Although the alkyl-group interaction has provisionally been interpreted as due to molecular "entanglement" in the liquid an alternative explanation in terms of restricted rotation of alkoxide groups is possible. This would require free rotation in the vapour and restricted rotation in the liquid, whilst the amount of rotation in the liquid should decrease with increase in alkyl chain length. Unfortunately, the published data on the dipole moments of these compounds are inconsistent and more accurate measurements are required before a decision can be made.

EXPERIMENTAL

The apparatus used and the methods of analysis and determination of b. p. of the alkoxides were as reported previously (*loc. cit.*).

Preparation of n-*Alkoxides of Titanium and Zirconium.*—The preparations of titanium ethoxide and zirconium ethoxide have been reported (Bradley, Hancock, and Wardlaw, *J.*, 1952, 2773; Bradley, Halim, Sadek, and Wardlaw, *J.*, 1952, 2032). The higher *n*-alkoxides were prepared by alcohol-interchange involving the *iso*propoxides by the methods previously described (*J.*, 1952, 2027, 4204, 5020). The results are summarised in the annexed Table.

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.[a]							
n-Propyl...	6·7	8·0	60	6·3	138°/0·5, 124°/0·1	16·87	16·85
n-Butyl ...	5·7	7·2	60	6·3	160°/0·8, 142°/0·1	14·10	14·07
n-Amyl ...	6·4	9·1	60	8·4	175°/0·8, 158°/0·1	12·16	12·09
n-Hexyl ...	6·1	10·3	65	9·3	193°/0·8, 176°/0·1	10·53	10·58
n-Heptyl	3·9	9·5	50	6·1	213°/0·4, 201°/0·1	9·42 †	9·42
n-Octyl ...	14·3	33·7	80	25·3	228°/0·5, 214°/0·1	8·52	8·48
Zirconium compounds.							
n-Propyl...	8·0	7·3	70	6·3 [b]	198°/0·03, 208°/0·1	27·85	27·85
n-Butyl ...	8·5	8·0	70	7·6 [c]	253°/0·3, 243°/0·1	23·8	23·8
n-Amyl ...	5·7	10·7	60	6·2 [b]	256°/0·01, 276°/0·1	20·8	20·75
n-Hexyl ...	9·7	20·4	80	12·0 [d]	310—320°/0·5—0·6 [e]	18·25	18·4
n-Heptyl	4·2	7·0	50	5·9 [b]	Dried at 170°/0·2 mm.	16·6 †	16·5
n-Octyl ...	6·3	10·7	40	9·9 [b]	„ 180°/0·2 mm.	15·1 †	15·0

[a] Mobile liquid. [b] Highly viscous liquid. [c] Solid. [d] Liquid slowly set to white solid. [e] Decomposition.

† The following carbon and hydrogen analyses were determined :

$Ti(OC_7H_{15})_4$:	Found : C, 66·3 ;	H, 11·9.	Reqd. :	C, 66·1 ;	H, 11·9%.
$Zr(OC_7H_{15})_4$	60·8	11·1		60·9	11·0
$Zr(OC_8H_{17})_4$	62·1	11·2		63·2	11·3

n-*Butyl Orthosilicate.*—Silicon tetrachloride (45 g.) was added dropwise to *n*-butyl alcohol (80 g.), and the liquid product aspirated for 2 hr. to remove hydrogen chloride. Volatile constituents were completely removed under reduced pressure, and the *n*-butyl orthosilicate obtained by distillation (b. p. 95—100°/0·1—0·2 mm.) as a colourless mobile liquid (75 g.) [Found : Si, 8·7. Calc. for $Si(OC_4H_9)_4$: Si, 8·8%], b. p. 115°/1·5, 118°/2·2, 121°/2·6, 127°/4·0, 129°/4·5, 134°/5·5, 137°/6·3, 140°/7·7, 143°/8·6, 149°/11·0, 161°/21, 188°/68, 194°/90, 202°/110, 213°/156, 235°/305, 268°/752 mm. $\log_{10}P$ (mm.) $= 8{\cdot}88 - 3246/T$; $L_v = 14{\cdot}84$ kcal./mole.

n-*Hexyl Orthosilicate.*—From the reaction involving silicon tetrachloride (45 g.) and *n*-hexyl alcohol (115 g.), *n*-hexyl orthosilicate (83·2 g.; b. p. 170°/0·8 mm.) was isolated as described for the *n*-butyl ester [Found : Si, 6·45. Calc. for $Si(OC_6H_{13})_4$: Si, 6·5%], b. p. 181°/1·75, 187°/2·5, 190°/2·9, 195·5°/4·5, 209°/8·0, 212°/9·0, 216°/11·0, 228°/18·5, 232°/21·0, 265°/76, 271°/80, 300°/250 mm. $\log_{10}P$ (mm.) $= 10{\cdot}33 - 4545/T$; $L_v = 21{\cdot}8$ kcal./mole.

Molecular Weights.—Determinations in benzene were carried out ebullioscopically in the apparatus previously described. Determinations in ethyl alcohol or *iso*propyl alcohol were made in a new apparatus by a method, to be described later, which involved weighing the solvent. In all cases the plot of Δt against concentration was linear within experimental error. Results are summarised in the annexed Table.

Vapour Densities.—Vapour density was evaluated by determining the amount of zirconium remaining in a flask (500 c.c.) after removal of the alkoxide at known temperature (*ca.* 50° above the b. p.) and pressure (*ca.* 10 mm.). Although these preliminary results are not accurate they nevertheless suggest that zirconium ethoxide and *iso*propoxide are probably monomeric in the vapour. Results were: $Zr(OEt)_4$: Found : *M*, 288. Calc. : *M*, 271. $Zr(OPr^i)_4$, Found : *M*, 384. Calc. : *M*, 327.

Alkoxide	Range of wts. (g.)	Solvent (c.c.)	*M*, found	*M*, calc.
$Ti(OC_2H_5)_4$	0·128—0·794	35·6 [a]	556	228·1
$Zr(OC_2H_5)_4$	0·090—0·907	35·3 [a]	980	271·5
$Zr(OC_4H_9)_4$	0·241—0·811	35·8 [a]	1290	383·7
$Ti(OC_5H_{11})_4$	0·167—1·116	36·2 [a]	565	396·5
$Zr(OC_5H_{11})_4$	0·567—1·785	35·7 [a]	1428	439·8
$Ti(OC_8H_{17})_4$	0·550—1·836	34·0 [a]	781	564·8
$Zr(OC_8H_{17})_4$	0·176—1·825	35·8 [a]	2046	608·1
$Zr(OC_2H_5)_4$	0·146—1·779	14·70 [b]	678	271·5
$Zr(OPr^i)_4,Pr^iOH$	0·090—0·734	18·21 [c]	732	387·6

[a] Benzene. [b] Ethyl alcohol (g.). [c] *iso*Propyl alcohol (g.).

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