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# METAL OXIDE ALKOXIDE (TRIALKYLSILYLOXIDE) POLYMERS

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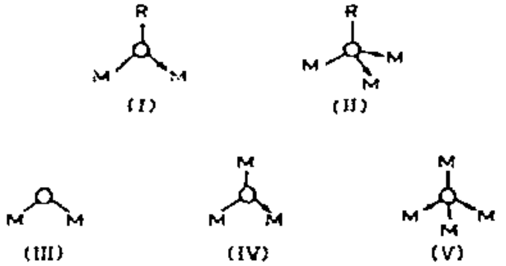
CONTENTS

## A. INTRODUCTION

The metal oxide alkoxides $[MO_x(OR)_{(y-2x)}]_n$, where M is a metal of valency $y$ and R is an alkyl group, are interesting polymeric compounds which bridge the gap between the oligomeric metal alkoxides $[M(OR)_y]_m$ and the macromolecular metal oxides $[M_2O_y]_\infty$. Structural aspects of the metal alkoxides have been reviewed by the author[1] whilst the metal oxides are well discussed in Well's textbook[2]. Similarly the metal oxide trialkylsilyloxides $[MO_x(OSiR_3)_{(y-2x)}]_n$ may be regarded as intermediate between the oligomeric metal trialkylsilyloxides $[M(OSiR_3)_y]_m$[3] and the mineral silicate macromolecules.

Both the metal alkoxides and the metal trialkylsilyloxides are coordination polymers by virtue of the tendency of the metal M to expand its coordination beyond its primary valency $y$ coupled with the ability of the alkoxide or trialkylsilyloxide oxygen to bridge two or more metal atoms (I, II, Fig. 1). Although it is obvious that the shape and size of a metal alkoxide coordination polymer must be related to the stereochemistry of the metal in its higher state of coordination



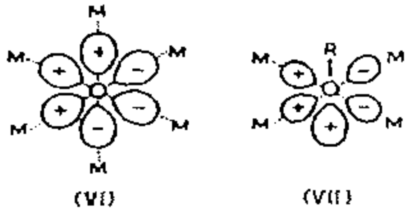


Fig. 1. Bridging by alkoxide and oxide ligands.
Fig. 2. "Non-classical" metal-oxygen bonds.

and the manner in which alkoxide groups will "cross-link" the metal–oxygen polyhedra there has been a dearth of X-ray structural data until recently[4] and there is still much to be learned in this field. In the metal oxide alkoxides the situation is further complicated by the fact that in addition to coordination polymerization due to bridging alkoxide groups there will be "condensation" polymerization involving primary metal–oxygen–metal bridges (III, Fig. 1) and coordination polymerization due to the oxide ligand (IV, V, Fig. 1). The bridging modes depicted in Fig. 1 all involve conventional localised $\sigma$-bonding by oxygen with digonal, trigonal and tetrahedral arrangements but these will not necessarily apply and other less familiar stereochemical distributions about the oxygen may occur. For example, although it is commonly assumed that the metal oxides MO with the sodium chloride structure are ionic, thus solving the problem of the octahedral coordination of the $O^{2-}$ ions, it is conceivable that there is some covalent bonding involving the p-atomic orbitals of oxygen (VI, Fig. 2) in polycentric molecular orbitals with either p- or d-atomic orbitals of the metal. Moreover, the peculiar stereochemistry of oxygen in lithium alkoxides[4] may be due to delocalized covalent bonding rather than ionic character. Examples of these "non-classical" types of oxygen bonds are shown in Fig. 2. In structure (VI) only the p-atomic orbitals of the $O^{2-}$ are shown but a contribution to polycentric bonding by the s-orbital is obviously possible. In structure (VII) the oxygen uses an sp-hybrid orbital to bond to the alkyl group leaving two p-orbitals and an sp-hybrid orbital for polycentric bonding with the metal atoms. There are two other factors which further complicate the structural picture. One is the steric effect of the alkoxide group which can be very marked in the case of tertiary and some secondary alkoxide groups and the larger trialkylsilyloxide groups. It has been well established in metal alkoxide chemistry that steric hindrance opposes coordination polymerisation and the same factor will arise in the metal oxide alkoxides although for a given alkyl group it will depend on the degree of hydrolysis $x$ in $MO_x(OR)_{(y-2x)}$. The second factor is the possibility of metal–oxygen double bond formation $M=O$ which will also diminish the degree of polymerization because it eliminates metal–oxygen–metal bridging. Metal oxygen double bonding seems to be restricted to the higher valencies of vanadium, chromium, manganese, niobium, molybdenum, tungsten, technetium, rhenium, ruthenium, osmium, and some of the actinides. It is thus clear that many interesting structural problems should arise in the metal oxide alkoxides and metal oxide trialkylsilyloxides.

Except for chromium(III) alkoxides and uranium hexatertiarybutoxide $U(OBu^t)_6$ the metal alkoxides containing lower aliphatic alkyl groups are generally easily hydrolysed to give metal oxide alkoxides.

$$M(OR)_y + xH_2O \rightarrow MO_x(OR)_{(y-2x)} + 2xROH \qquad (1)$$

The metal trialkylsilyloxides appear to hydrolyse rather more slowly but there are no major difficulties in preparing the metal oxide trialkylsilyloxide. Earlier work in the metal oxide alkoxide and metal oxide trialkylsilyloxide fields was reviewed by the author[5] and the present article will deal exclusively with the results of the author and his coworkers. The reason for so doing is that few if any other comparable studies have been made under such carefully controlled and standardized conditions.

Most work has been carried out with Group IV and Group V metal derivatives with some studies on cerium(IV), uranium(V) and aluminium derivatives. The results were obtained by controlled hydrolysis of the metal alkoxide in a boiling solution of the appropriate alcohol in an ebulliometer. This enabled the degree of polymerization $n$ in $[MO_x(OR)_{(y-2x)}]_n$ to be obtained for a large number of compounds in which the degree of hydrolysis $x$ was increased from zero to a value which caused precipitation of insoluble products. Analysis and infrared spectroscopy was also carried out on soluble products to check that no M–OH bonds were present.

## B. GENERAL STRUCTURAL THEORY

Before dealing with individual compounds it is instructive to consider the general conclusions which have developed from the interpretation of molecular weight data on a number of metal oxide alkoxide polymer systems[7–13]. The results showed, as expected, that an increase in the degree of hydrolysis $x$ was accompanied by an increase in the number average degree of polymerization $n$. However, the variation of $n$ with $x$ showed a characteristic pattern which was interpreted in terms of structures for the individual metal oxide alkoxides. It was found that each alkoxide $[M(OR)_y]_p$ gave rise to a series of polymeric oxide alkoxides which was determined by the value of $q$ the number of M–O–M links between adjacent $M_pO_q$ units in the structure. It was shown by Bradley and Holloway[13] that in such a polymer series a simple linear relationship was given between the reciprocal of $n$ and the value of $x$:

$$n^{-1} = p^{-1} - q^{-1}x \qquad (2)$$

An interesting feature of the structural series was the fact that the number average degree of polymerization was independent of polymer distribution provided that all polymers conformed to the structural series. Thus the value of $n$ was determined uniquely by $x$ although at any given value of $x$ (*e.g.* non-integral) there could be present several species with different $n$'s and $x$'s. In principle, if the degree of polymerization $p$ of the parent alkoxide $[M(OR)_y]_p$ is known and a structure assigned to the molecule then by inspection it should be possible to deduce a likely value for $q$ and hence the structures of the derived metal oxide alkoxides. The remainder of the review will deal with results obtained first on metal oxide alkoxides and then metal oxide trialkylsilyloxides.

## C. METAL OXIDE ALKOXIDES

For convenience this section will be subdivided according to the oxidation number of the metal involved.

### (i) *Quadrivalent metals*

Studies have been made on the hydrolysis of the alkoxides of titanium(IV)[6,7,8], zirconium(IV)[9,10], tin(IV)[13] and cerium(IV)[13].

*(a) Titanium oxide alkoxides.* Since titanium tetramethoxide is practically insoluble in methanol this system could not be studied. Bradley, Gaze and Wardlaw[7] found that titanium tetraethoxide was almost trimeric ($p = 2.91$ at a concentration of 0.767 mole/kg) and that the titanium oxide ethoxide system was close to the $p_3q_4$ polymer series. Thus the experimental data give a straight line $n^{-1}_{\text{exp.}} = 0.346 - 0.260x$ which may be compared with the theoretical $n^{-1} = 0.333 - 0.250\,x$. Caughlan *et al.*[18] proposed two possible structures for $Ti_3(OEt)_{12}$ based on octahedrally coordinated titanium and one of these (Fig. 3) was adopted by Bradley *et al.*[7] as a basis for the $p_3q_4$ polymer series. Inspection of the trimer structure shows that there are two obvious ways in which crosslinking could lead to a polymer series (Fig. 4). In 4(a) crosslinking involving a terminal octahedral

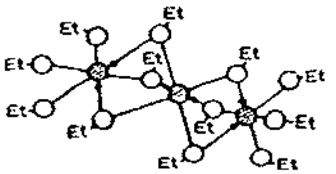


Fig. 3. $Ti_3(OEt)_{12}$ with octahedral titanium.

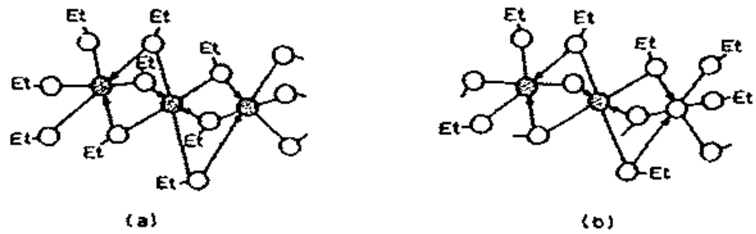


Fig. 4. (a) Crosslinking for the $p_3q_3$ polymer series. (b) Crosslinking for the $p_3q_4$ polymer series.

face from each trimer unit would lead to a $p_3q_3$ polymer series whereas crosslinking by the tri-octahedral edge (4b) would give the observed $p_3q_4$ series. The $p_3q_4$ polymer series corresponds to a family of titanium oxide ethoxides having the general formula $[Ti_{3(x+1)}O_{4x}(OEt)_{4(x+3)}]$, *i.e.* $Ti_3(OEt)_{12}$; $Ti_6O_4(OEt)_{16}$; $Ti_9O_8(OEt)_{20}$; $Ti_{12}O_{12}(OEt)_{24}$ ...... $[Ti_3O_4(OEt)_4]_\infty$. In fact the compound $Ti_6O_4(OEt)_{16}$ (Fig. 5) readily crystallized from alcoholic solution when approximately 0.5 g.mole of water was added per g.mole $Ti(OEt)_4$ and its molecular weight in benzene solution was in good agreement with the calculated value. The next member of the series $Ti_9O_8(OEt)_{20}$ was not isolated but the compound $Ti_{12}O_{12}(OEt)_{24}$ was obtained and recrystallized with difficulty. Further evidence for the $p_3q_4$ polymer series resulted from thermolysis studies on $Ti_6O_4(OEt)_{16}$. Heating to 200° *in vacuo* caused disproportionation into the volatile $Ti(OEt)_4$ and left a non-volatile residue which was insoluble and reasonably near in analysis to the limiting infinite polymer $[Ti_3O_4(OEt)_4]_\infty$.

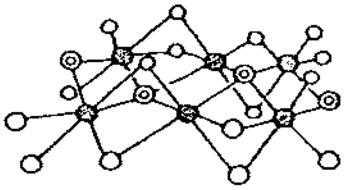
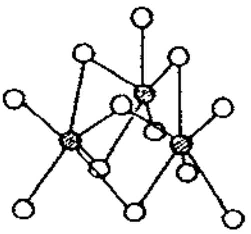


Fig. 5. $Ti_6O_4(OEt)_{16}$ ● = Ti; ⊚ = Oxygen in TiOTi; ○ = Oxygen in TiOEt (Et groups omitted).

$$Ti_6O_4(OEt)_{16} \rightarrow Ti_3O_4(OEt)_4 + 3\,Ti(OEt)_4 \qquad (3)$$

The infinite polymer would certainly be expected to be non-volatile and insoluble.

An interesting feature of the $p_3q_4$ polymer series is the stereochemistry of the oxide ligands which are arranged apically in tetragonal pyramids with basal titanium atoms and this has led to scepticism concerning the proposed structure of the titanium oxide ethoxides[19]. Martin and Winter[19] suggested the possibility that the structure of $Ti_3(OEt)_{12}$ would be based on a trigonal prism configuration



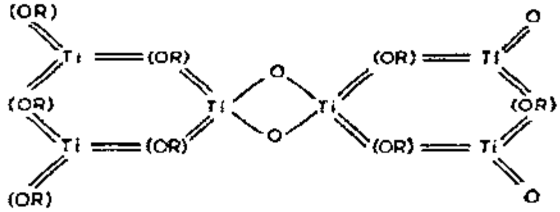
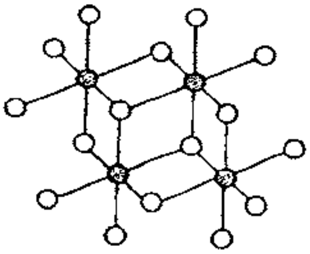


Fig. 6. Ti$_3$(OR)$_{12}$ ● = Ti; ○ = Oxygen in ROTi (R groups omitted) with trigonal prismatic titanium.

Fig. 7. Postulated structure for Ti$_4$O$_4$(OEt)$_{16}$.

for titanium (Fig. 6) and that Ti$_6$O$_4$(OEt)$_{16}$ would have a structure (Fig. 7) involving some terminal Ti = O groups. However, infrared spectra on Ti$_6$O$_4$(OEt)$_{16}$ and Ti$_{12}$O$_{12}$(OEt)$_{24}$ conclusively ruled out the presence of Ti = O groups[20] and a subsequent X-ray structural analysis of crystalline titanium tetraethoxide has revealed that it is tetrameric with octahedral titanium[4] (Fig. 8a). Barraclough *et al.*[21a] have claimed that significant concentrations of tetramer are present in solution. Extremely careful cryoscopic studies by Bradley and Holloway[21b] nevertheless reaffirmed the trimeric behaviour of the tetraethoxide in solution over a wide concentration range and it seems that the structure of titanium tetraethoxide depends on its environment. Therefore, it would not be surprising if the structure of crystalline Ti$_6$O$_4$(OEt)$_{16}$ were different from that postulated (Fig. 5) in solution. In fact it would be predicted that the tetrameric ethoxide would give a $p_4q_4$ polymer series [Ti$_{(4+x)}$O$_x$(OEt)$_{2(8+x)}$] with $n^{-1} = 0.25 - 0.25\,x$ which clearly does not accord with results in solution. However, it is possible that the $p_3q_4$ species Ti$_6$O$_4$(OEt)$_{16}$ might crystallize into the $p_4q_4$ species Ti$_{12}$O$_8$(OEt)$_{32}$. Obviously this point can only be settled by an X-ray diffraction analysis of the crystalline derivative. Watenpaugh and Caughlan[25] have determined the structure of a product claimed to be Ti$_7$O$_5$(OEt)$_{19}$ and the Ti$_7$O$_{24}$ molecular unit (Fig. 8b) is obviously related to the Ti$_4$O$_{16}$ unit found by Ibers for the tetraethoxide.



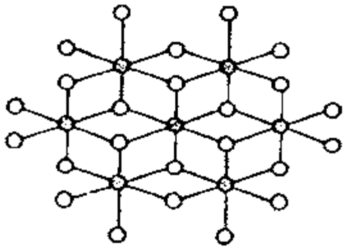
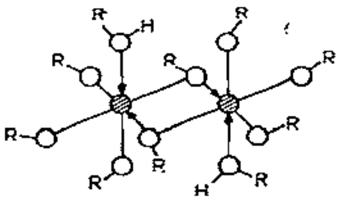


Fig. 8(a) Ti$_4$(OEt)$_{16}$ ● = Ti; ○ = Oxygen in EtOTi (Et groups omitted).
Fig. 8(b) Ti$_7$O$_{24}$ ● = Ti; ○ = Oxygen.

Bradley, Gaze and Wardlaw[8] found that in more dilute ethanolic solutions titanium tetraethoxide was significantly less polymeric ($p = 2.40$ at 0.185g mole/kg;



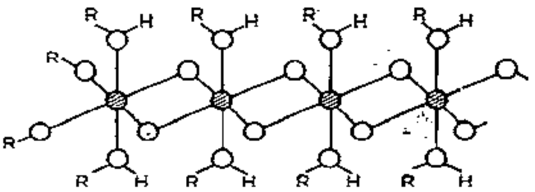


Fig. 9. $Ti_2(OR)_8$, 2ROH.
Fig. 10. $p_1q_2$ Polymer.

$p = 2.30$ at 0.0425 g mole/kg) and it was suggested that this was due to solvation giving a dimeric species $Ti_2(OEt)_8$, $(EtOH)_2$ (Fig. 9). This could lead to a $p_2q_3$ polymer series $[Ti_{2(z+1)}O_{3z}(OEt)_{2(z+4)}$, $(EtOH)_{2(z+1)}]$ with $n^{-1} = 0.5–0.33\ x$. Bradley and Holloway[13] have shown that if two polymer series $p_aq_r$ and $p_bq_s$ are simultaneously present with the proportion of metal atoms in the $p_aq_r$ series equal to $\alpha$ and the proportion in the $p_bq_s$ series equal to $(1-\alpha)$, then:

$$n^{-1} = [\alpha p_a^{-1}+(1-\alpha)p_b^{-1}]-[\alpha q_r^{-1}+(1-\alpha)q_s^{-1}]_x \tag{4}$$

Thus if $\alpha$ remains constant over the hydrolysis range studied the $n^{-1}$ *vs.* $x$ relationship will still be linear and the intercept $n^{-1}$ at $x = o$ can be used to evaluate $\alpha$. The validity of the model can then be checked by using the value of $\alpha$ to calculate the slope. Applying this method to the experimental data $n^{-1}_{\text{exp.}} = 0.346–0.260\,x$ obtained at the highest concentration and solving for a mixture of $p_3q_4$ with $p_2q_3$ polymer series gives the result that 92.4% of the titanium ($\alpha = 0.924$) is in the $p_3q_4$ series. This value of $\alpha$ leads to a calculated slope of $-0.257$ in good agreement with the experimental value of $-0.260$. For the lower initial concentrations of titanium tetraethoxide the line $n^{-1}_{\text{exp.}} = 0.41-0.30x$ is obtained corresponding to $\alpha = 0.55$ and a calculated slope of $-0.29$. Thus a very good correlation with the molecular weight studies is obtained in terms of two structural series for the titanium oxide ethoxides in boiling ethanolic solution.

Although titanium tetra *n*-propoxide is trimeric in solution in freezing benzene[21] it was found by Bradley, Gaze and Wardlaw[8] that in boiling *n*-propanol the degree of polymerization was 1.64. The latter could be due to depolymerization at the higher temperature or to extensive solvation involving both a dimer $Ti_2(OPr^n)_8$, $(Pr^nOH)_2$ and the octahedral monomer $Ti(OPr^n)_4$, $(Pr^nOH)_2$. Hydrolysis of the solvated dimer should give the $p_2q_3$ polymer series and the solvated monomer might be expected to give a $p_1q_2$ polymer series (Fig. 10). From the degree of polymerization of the "unhydrolysed" tetra *n*-propoxide it may be calculated that 78% of the titanium is present as the dimer and 22% as monomer and therefore a mixture of 78% $p_2q_3$ and 22% $p_1q_2$ series would require $n^{-1} = 0.61–0.37x$. The experimental data gave a reasonable straight line with $n^{-1} = 0.61-0.42x$. The data obtained with other titanium alkoxides in their corresponding alcohols was less accurate and less extensive than for the ethoxide and is not amenable to

TABLE 1

TITANIUM OXIDE ALKOXIDES

| *Alkoxide* | $N_0$* | *Exptl. equation* | $\%p_3q_4$ | $\%p_2q_3$ | $\%p_1q_2$ | *Slope of Equation* | |
|---|---|---|---|---|---|---|---|
| | | | | | | *Calc.* | *Exptl.* |
| $Ti(OEt)_4$[a] | 2.91 | $n^{-1} = 0.346 - 0.260x$ | 92.4 | 7.6 | 0 | −0.257 | −0.260 |
| $Ti(OEt)_4$[b] | 2.35 | $n^{-1} = 0.41 - 0.30x$ | 55 | 45 | 0 | −0.29 | −0.30 |
| $Ti(OPr^n)_4$[c] | 1.64 | $n^{-1} = 0.61 - 0.42x$ | 0 | 78 | 22 | −0.37 | −0.42 |

* $N_0$ — Initial degree of polymerization of $Ti(OR)_4$ in boiling ROH.
[a] = concn. 0.767 g.mol./kg.; [b] = concn. 0.185 and 0.0425 g.mol./kg.; [c] = concn. of 0.144 g.mol./kg.

structural analysis. However, the ebulliometric studies in the higher boiling alcohols gave some peculiar results which may indicate reversibility of the hydrolysis under those conditions. The results and conclusions for $[TiO_x(OEt)_{(4-2x)}]_n$ and $[TiO_x(OPr^n)_{(4-2x)}]_n$ are summarised in Table 1. It is noteworthy that in all of the structures postulated for the titanium oxide alkoxides the titanium is octahedrally 6-coordinated. It was thought that zirconium might exhibit a higher coordination number and therefore the hydrolysis of zirconium alkoxides was studied under conditions closely similar to those described for titanium alkoxides.

TABLE 2

ZIRCONIUM OXIDE ALKOXIDES

| *Alkoxide* | $N_0$* | *Exptl. equation* | $\%p_3q_4$ | $\%p_2q_3$ | $\%p_1q_2$ | *Slope of Equation* | |
|---|---|---|---|---|---|---|---|
| | | | | | | *Calc.* | *Exptl.* |
| $Zr(OEt)_4$[a] | 2.24 | $n^{-1} = 0.377 - 0.266x$ | 73.8 | 26.2 | 0 | −0.272 | −0.266 |
| $Zr(OEt)_4$[b] | 2.17 | $n^{-1} = 0.405 - 0.302x$ | 57.0 | 43.0 | 0 | −0.286 | −0.302 |
| $Zr(OEt)_4$[c] | 2.10 | $n^{-1} = 0.430 - 0.305x$ | 42.0 | 58.0 | 0 | −0.298 | −0.305 |
| $Zr(OPr^n)_4$[d] | 2.44 | $n^{-1} = 0.403 - 0.24x$ | 58.0 | 42.0 | 0 | −0.285 | −0.24 |
| $Zr(OBu^n)_4$[e] | 1.77 | $n^{-1} = 0.564 - 0.323x$ | 0 | 87.2 | 12.8 | −0.355 | −0.323 |
| $Zr(OPr^i)_4$[f] | 1.91 | $n^{-1} = 0.466 - 0.272x$ | 20.4 | 79.6 | 0 | −0.316 | −0.272 |
| $Zr(OBu^t)_4$ | 1.94 | $n^{-1} = 0.476 - 0.333x$ | 14.4 | 85.6 | 0 | −0.321 | −0.333 |

* $N_0$ = Initial degree of polymerization of $Zr(OR)_4$ in boiling ROH.
Alkoxide concentrations: [a] = 0.723; [b] = 0.409; [c] = 0.186; [d] = 0.147; [e] = 0.0707; [f] = 0.382; [g] = 0.101 g.mol./kg.

*(b) Zirconium oxide alkoxides.* In Table 2 are presented the results obtained by Bradley and Carter[9,10] re-evaluated in terms of the relationship between $n^{-1}$ and $x$. In the case of zirconium tetraethoxide the initial degree of polymerization $n_0$ varied slightly with concentration and at each concentration the points for $x = 0$ to $\sim 0.2$–$0.3$ were definitely deviating from the straight line found for $x = 0.2$ to $\sim 1.0$. In addition to the deviations for $x < 0.2$–$0.3$ another puzzling feature of the results was that the $n_0$ values for $Zr(OEt)_4$ were lower than for $Ti(OEt)_4$ at comparable concentrations. These anomalies were discussed in detail by Bradley and Carter[9] but they were only able to speculate on possible causes.

The linear portions of the $n^{-1}$ *versus* $x$ curves gave (Table 2) reasonable confirmation that the zirconium oxide ethoxides were present as mixtures of the $p_3q_4$ and $p_2q_3$ polymer series and it thus appears that zirconium is octahedrally 6-coordinated in these compounds. Less data were obtained on the hydrolysis of $Zr(OPr^n)_4$ and $Zr(OBu^n)_4$ but in both cases a reasonably linear relationship between $n^{-1}$ and $x$ was obtained. The agreement between observed and calculated slopes suggests that zirconium oxide n-propoxides exist as a mixture of $p_3q_4$ and $p_2q_3$ polymer series whilst zirconium oxide n-butoxides exist as a mixture of $p_2q_3$ and $p_1q_2$ polymer series. Even more interesting were the results for $Zr(OBu^i)_4$ which actually forms a crystalline solvate $Zr(OBu^i)_4$, $Bu^iOH$ and lends credence to the solvation hypothesis. The value of $n_o = 1.52$ suggested the presence of both $Zr_2(OBu^i)_8$, $(Bu^iOH)_2$ and $Zr(OBu^i)_4$, $(Bu^iOH)_2$ in boiling isobutanol solution but the plot of $n^{-1}$ *versus* $x$ was curved in the sense that increase in $x$ caused an increase in the proportion of the $p_1q_2$ series. Therefore the data could not be interpreted in terms of the polymer series.

Another solvated alkoxide was the tetra isopropoxide which exists as the dimeric species $Zr_2(OPr^i)_8$, $(Pr^iOH)_2$ corresponding to the postulated structure in Fig. 9. Hydrolysis of zirconium isopropoxide[10] gave a linear variation of $n^{-1}$ with $x$ and reasonable agreement between the observed and calculated slopes for a mixture of predominantly the $p_2q_3$ polymer series with some of the $p_3q_4$ series. Slightly better results along the same lines were also obtained with zirconium sec-butoxide which also forms a solvate. The behaviour of $Zr_2(OPr^i)_8$, $(Pr^iOH)_2$ and $Zr_2(OB^s)_8$, $(Bu^sOH)_2$ constituted the strongest evidence for the solvated polymer series $p_2q_3$. It was therefore of added interest to investigate the behaviour of stannic isopropoxide which also forms a dimeric solvate $Sn_2(OPr^i)_8$, $(Pr^iOH)_2$.

*(c) Stannic oxide isopropoxides.* The hydrolysis of stannic isopropoxide in boiling isopropanol was investigated by Bradley and Holloway[13] who had developed a more accurate ebulliometric method than had been used for the work on titanium or zirconium alkoxides. The results are presented in Table 3 and it is clear that the stannic oxide isopropoxides come very close in behaviour to the predictions of a $p_2q_3$ polymer series with a small but significant proportion of the $p_1q_2$ polymer series. In fact the results definitely show that the monomeric species

TABLE 3

STANNIC AND CERIC OXIDE ISOPROPOXIDES

| *Alkoxide* | $N_o$* | *Exptl. Equation* | $\%p_2q_3$ | $\%p_1q_2$ | *Slope of Equation* | |
|---|---|---|---|---|---|---|
| | | | | | *Calc.* | *Exptl.* |
| $Sn_2(OPr^i)_8$, $(Pr^iOH)_2$[a] | 1.85 | $n^{-1} = 0.5505 - 0.3751x$ | 89.9 | 10.1 | −0.350 | −0.375 |
| $Ce_2(OPr^i)_8$, $(Pr^iOH)_2$[b] | 1.86 | $n^{-1} = 0.5358 - 0.3608x$ | 92.8 | 7.2 | −0.346 | −0.361 |

* $N_o$ = Initial degree of polymerization of $M(OPr^i)_4$ in boiling $Pr^iOH$.
Alkoxide concentrations: [a] = 0.264 and 0.310; [b] = 0.109; 0.127; 0.173 and 0.205 g.mol./kg.

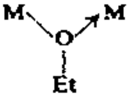
conform to the $p_1q_2$ series rather than an alternative $p_1q_3$ series which would require a slope of $-0.333$. Not only did this work give strong support to the solvated $p_2q_3$ polymer series but it showed that the theory applied to a non-transition metal too.

*(d) Ceric oxide isopropoxides.* The other metal alkoxide known to form a solvated dimer was cerium(IV) isopropoxide and its hydrolysis in boiling isopropanol was studied by Bradley and Holloway[13]. From the results in Table 3 it is evident that the ceric oxide-isopropoxides also behave predominantly as $p_2q_3$ polymers with a small mixture of the $p_1q_2$ series. Accordingly it seems that Ce(IV) is also octahedrally 6-coordinated in the ceric oxide isopropoxides in spite of the known tendency for cerium to exhibit the coordination number of 8. However, two important points must be borne in mind in interpreting these data. Firstly, it is possible that the structures of the metal oxide alkoxides may be dependent on environment and these experiments were carried out in solutions of the boiling alcohols. It could well be that in the solid products the structures are different and might involve higher coordination numbers. Secondly, the deduction of the metal coordination number for species in boiling alcoholic solutions is much less sure than deductions based on the degree of polymerization of a metal alkoxide in a hydrocarbon (non-donor) solvent. For example, if $Ce(OPr^i)_4, Pr^iOH$ is dimeric in cyclohexane it is very reasonable to assume that the cerium is octahedrally coordinated and that the complex has the same structure as shown in Fig. 9 for $Ti_2(OR)_8, (ROH)_2$. In boiling isopropanol we do not know that the same structure will occur because there is always the possibility that in the presence of the vast excess of alcohol donor molecules a higher coordination could be attained as for example in $Ce_2(OPr^i)_8, (Pr^iOH)_6$ which would fit an 8-coordinated structure.

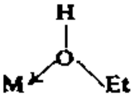
In the case of titanium oxide ethoxides there is less room for doubt for the following reasons.

To date there has been no example of 8-coordinated titanium involving titanium–oxygen bonds and the structure of solid titanium tetraethoxide is definitely known to contain octahedrally coordinated titanium. In addition, the degree of polymerization of titanium tetraethoxide is practically the same in hydrocarbon solvents as it is in boiling ethanol and two of the titanium oxide ethoxides were examined in benzene solution and found to have practically the same molecular weights as in boiling ethanol. We cannot be so sure of the zirconium oxide ethoxides. The structure of zirconium tetraethoxide has not yet been determined but in benzene it has a slightly higher degree of polymerization than titanium tetraethoxide and this could be due either to $Zr(OEt)_4$ containing octahedrally coordinated tetramers (*viz.* Fig. 8) in addition to trimers or possibly to the presence of higher polymers containing 8-coordinated zirconium. It is certainly most odd that in boiling ethanol solution the titanium tetraethoxide has a higher degree of polymerization than has zirconium tetraethoxide at a comparable concentration.

It could be that the more highly solvated zirconium compound has 8-coordinated zirconium although this seems to imply that the greater stability of



bridges relative to



coordination is greater for titanium than zirconium. In the case of zirconium isopropoxide we are on surer ground because the solvated species $Zr(OPr^i)_4, Pr^iOH$ is readily isolated in crystalline form and it is dimeric in benzene and practically dimeric in boiling isopropanol and there is no reason to doubt the 6-coordinated structure (Fig. 9) in this case. In the zirconiumoxide–isopropoxides the first two points ($x < 0.3$) deviated significantly from the $n^{-1}$ *versus* $x$ line suggesting that as the degree of hydrolysis is increased the proportion of $p_3q_4$ polymers rapidly increases from zero (at $x = 0$) to about 20% ($x > 0.3$). This is understandable in terms of steric factors. Thus the steric hindrance of isopropoxide groups opposes polymerization to the trimeric $Zr_3(OPr^i)_{12}$ and in the presence of isopropanol the solvated species $Zr_2(OPr^i)_8, (Pr^iOH)_2$ is sterically more favoured. In the oxide isopropoxides the proportion of isopropoxide groups to zirconium atoms decreases with increase in degree of hydrolysis and relaxes the steric hindrance thus favouring the $p_3q_4$ polymer series. It is noteworthy that zirconium sec-butoxide behaves similarly and in the oxide sec-butoxide polymers there is a slightly smaller proportion of the $p_3q_4$ series no doubt due to the slightly greater steric hindrance by sec-butoxide groups.

### *(ii) Quinquevalent metals*

Studies have been made on the hydrolysis of the alkoxides of niobium(V)[22], tantalum(V)[11,12] and uranium(V)[13] in the boiling alcohol solution.

*(a) Tantalum oxide alkoxides.* The tantalum penta alkoxides are dimeric in hydrocarbon solvents and proton magnetic resonance studies[23] have confirmed the structure in Fig. 11 of two octahedra sharing a common edge. Therefore a test

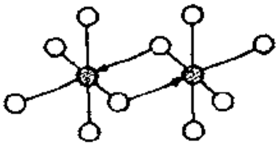


Fig. 11. $M_2(OR)_{10}$ ● = Nb or Ta; ○ = Oxygen in OR (R groups omitted).

of the structural theory is possible because it would be reasonable to expect a $p_2q_3$ polymer series of unsolvated tantalum oxide alkoxides $[Ta_{2(x+1)}O_{3x}(OR)_{2(x+5)}]$ to be formed analogous structurally to the solvated series $[M_{2(x+1)}O_{3x}(OR)_{2(x+4)}$,

$(ROH)_{2(x+1)}$] postulated for some of the quadrivalent metals. In fact the tantalum penta alkoxides are significantly less than dimeric in the boiling alcohol solution and this suggested the presence of an octahedral solvated monomer $Ta(OR)_5$, ROH which might introduce $p_1q_1$, $p_1q_2$ or $p_1q_3$ oxide alkoxide polymers. Fortunately tantalum penta methoxide is soluble in methanol and was thus amenable to hydrolytic polymerization studies. The plot of $n^{-1}$ *versus* $x$ gave a good straight line and, as the data in Table 4 show, there is quantitative agreement for a mixture of 85.6% $p_2q_3$ and 14.4% $p_1q_2$ polymer series. For tantalum oxide ethoxides there was a slightly higher percentage of the $p_2q_3$ series (91%) and better agreement between the observed and calculated slope was given if the remaining 9% was in a $p_1q_1$ polymer series. In the $p_1q_1$ series there will be only one Ta–O–Ta bridge between adjacent octahedral units in the polymer. As a further check on the validity of the $p_2q_3$ series some of the tantalum oxide ethoxides were isolated and molecular weights measured in benzene to prevent solvation. The results agreed within the experimental error with the requirements of the $p_2q_3$ structural series. For tantalum oxide *n*-propoxides good agreement was found (Table 4) for a mixture of the $p_2q_3$ series (72.4%) and the $p_1q_2$ series (27.6%) and it was interesting to note the lower proportion of the $p_2q_3$ series in this case which was probably due to the higher boiling point of n-propanol. In the hydrolysis of tantalum penta sec-butoxide an interesting example of the effect of steric hindrance was observed. The steric effect of the sec.-butoxide groups prevents dimerization of $Ta(OBu^s)_5$ which is practically monomeric both in benzene and in the boiling alcohol. However, it is possible that the solvated monomer $Ta(OBu^s)_5$, $Bu^sOH$ could be formed in the alcohol and this would be expected to give rise to a $p_1q_1$ or $p_1q_2$ or $p_1q_3$ series of tantalum oxide sec-butoxides. In fact the plot of $n^{-1}$ *versus* $x$ gave pronounced curvature in the region $x = 0$ to $0.35$ followed by a linear portion for $x = 0.35$ to $1.3$. This behaviour was interpreted as showing that the tantalum oxide sec-butoxides gave a mixture of the $p_1q_2$ and $p_2q_3$ series with the proportion of the latter rising rapidly from 13.1% at $x = 0$ to 28.6% at $x = 0.35$ where the $n^{-1}$ *vs.* $x$ curve begins to be linear. Thus as the degree of hydrolysis increased with

TABLE 4

TANTALUM AND URANIUM(V) OXIDE ALKOXIDES

| *Alkoxide* | $N_0$* | *Exptl. equation* | %$p_2q_3$ | %$p_1q_2$ | *Slope of Equation* | |
|---|---|---|---|---|---|---|
| | | | | | *Calc.* | *Exptl.* |
| $Ta_2(OMe)_{10}$ | 1.76 | $n^{-1} = 0.5721 - 0.3929x$ | 85.6 | 14.4 | −0.357 | −0.393 |
| $Ta_2(OEt)_{10}$ | 1.85 | $n^{-1} = 0.5458 - 0.3389x$ | 90.8 | (9.2)** | −0.333 | −0.339 |
| $Ta_2(OPr^n)_{10}$ | 1.59 | $n^{-1} = 0.6382 - 0.3838x$ | 72.4 | 27.6 | −0.379 | −0.384 |
| $U_2(OEt)_{10}$ | 1.48 | $n^{-1} = 0.6755 - 0.3841x$ | 64.9 | 35.1 | −0.392 | −0.384 |

$N_0$* = Initial degree of polymerization of $M(OR)_5$ in boiling ROH.
** = % of metal in $p_1q_1$ polymer series.

the accompanying loss of Ta–OBu$^t$ groups the steric hindrance to coordination polymerization is lessened leading to an increase in proportion of the tantalum species in the $p_2q_3$ polymer series. Summarizing the results on the tantalum oxide alkoxides there appears to be strong support for the existence of the $p_2q_3$ polymer series together with some $p_1q_2$ polymers. The evidence for $p_1q_3$ polymers in the tantalum oxide ethoxide system instead of $p_1q_2$ is not overwhelming because of the high percentage of the $p_2q_3$ series which dominates the equation and renders discrimination between the alternative $p_1q_2$ and $p_1q_3$ series difficult. Therefore it is possible that all of the tantalum oxide alkoxides give a mixture of the $p_2q_3$ and $p_1q_2$ polymer series.

*(b) Niobium oxide alkoxides.* Since niobium penta alkoxides are also dimeric with the structure shown[23] in Fig. 11 it was expected that the niobium oxide alkoxides would resemble the corresponding tantalum derivatives. However, since it is known that niobium has a slightly greater tendency to form $M = O$ bonds than tantalum there was also the possibility that different behaviour would be found. Bradley and Holloway[22] have studied the hydrolysis of niobium penta alkoxides but the work is not yet complete. For niobium oxide methoxides the behaviour was indeed very similar to that of the tantalum compounds in giving a mixture of the $p_2q_3$ and $p_1q_2$ polymer series. For the higher homologues the behaviour was a little different and work is still in progress to check whether this is due to to the formation of Nb=O bonds. It is relevant to mention at this point that vanadium forms a series of monomeric vanadyl trialkoxides $O{=}V(OR)_3$ which can be distilled *in vacuo*.

*(c) Uranium(V) oxide ethoxides.* Uranium penta ethoxide is another example of a dimeric structure $U_2(OEt)_{10}$ and it was of interest to compare the uranium-oxide ethoxides with the tantalum oxide ethoxides. The results of Bradley and Holloway[13] are summarised in Table 4. It is especially noteworthy that $U_2(OEt)_{10}$ has a lower degree of polymerization in boiling ethanol than has $Ta_2(OEt)_{10}$ suggesting greater solvation of the uranium compound. This calls to mind the difference between $Ti(OEt)_4$ and $Zr(OEt)_4$ in boiling ethanol. The uranium oxide ethoxides gave a very good linear correlation between $n^{-1}$ and $x$ over the whole range of $x = 0$ to 1.5 and left no doubt that a mixture of the $p_2q_3$ (64.9%) and $p_1q_2$ (35.1%) polymer series was present. With the relatively low percentage of the $p_2q_3$ polymer series present it was much easier to distinguish between the $p_1q_2$ and $p_1q_3$ series as candidates for the monomer series and the results came out clearly in favour of the $p_1q_2$ series. Therefore it seems that uranium also prefers octahedral coordination in its oxide ethoxides although it is known to exhibit 8-coordination with some oxygen containing ligands. Unfortunately, uranium penta methoxide is sparingly soluble in boiling methanol and this precluded a study of its hydrolytic polymerization. This was particularly disappointing because

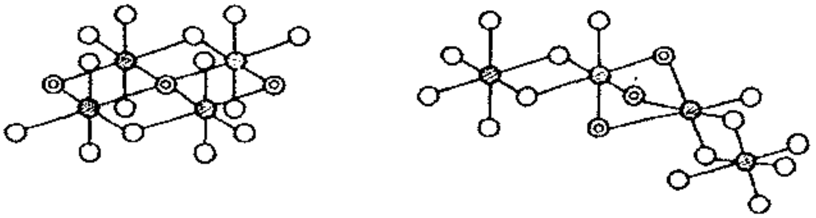
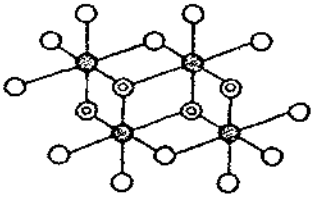


Fig. 12. $M_4O_3(OR)_{14}$ ● = M; ⊚ = Oxygen in MOM; ○ = Oxygen in OR groups.

$U(OMe)_4$ in trimeric in benzene[1] and it was expected that the uranium-oxide methoxides would show different behaviour from the uranium oxide ethoxides.

Before leaving the quinquevalent elements it should be pointed out that the $p_2q_3$ polymer series is not unique structurally because, as shown in Fig. 12 for $M_4O_3(OR)_{14}$ for example, there are different ways in which dimer units may be crosslinked by three M–O–M bridges. Therefore our molecular weight studies only reveal the average molecular size and cannot exactly define the structure of the polymer.

Another interesting point involves the $p_2q_4$ polymer series in which adjacent dimer units are crosslinked by four M–O–M bridges as shown in Fig. 13. This would lead to the relationship $n^{-1} = 0.5 - 0.25\,x$, but as the data in Table 4 show there is no evidence to suggest that this polymer series is present in any of the systems which have been studied.



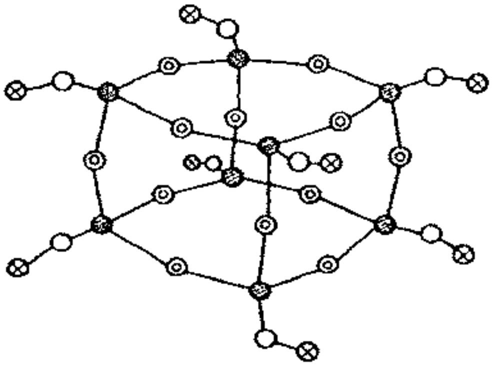


Fig. 13. $M_4O_4(OR)_{12}$ ● = M; ⊚ = Oxygen in MOM; ○ = Oxygen in OR groups.
Fig. 14. $Ti_8O_{12}(OSiMe_3)_8$ ● = Ti; ⊚ = Oxygen in TiOTi, ○ = Oxygen in TiOSi; ⊗ = $SiMe_3$ group.

### *(iii) Tervalent metals*

Studies on the hydrolysis of aluminium tri-isopropoxide in boiling isopropanol have been carried out[22] and a linear relationship between $n^{-1}$ and $x$ was found. However, more work is required before the parameters of the equation can be unambiguously related to structural models. Adams *et al.*[22a] found that hydrolysis of ferric alkoxides leads to a decrease in the paramagnetic susceptibility but molecular weights were not determined on the products.

### D. METAL OXIDE TRIALKYLSILYLOXIDES

The hydrolysis of metal trialkylsilyloxides $[M(OSiR_3)_y]_m$ forms compounds $[MO_x(OSiR_3)_{(y-2x)}]_n$ known as metal oxide trialkylsilyloxides or polyorganosiloxanometalloxanes. Early work in this field was carried out by Andrianov and co-workers[24] who obtained interesting polymeric products on aluminium and titanium derivatives. Unfortunately their work did not probe very deeply into the structural aspects of this class of compound and the remainder of this review will deal exclusively with the systematic studies of Bradley and Prevedorou–Demas[14–17].

A major distinction between metal alkoxides and metal trialkylsilyloxides involves their different susceptibilities to hydrolysis. Most of the metal alkoxides are prone to rapid hydrolysis whereas the hydrolysis of metal trialkylsilyloxides is perceptibly slower.

$$M(OSiR_3)_y + xH_2O \xrightarrow{\text{slow}} MO_x(OSiR_3)_{(y-2x)} + 2xR_3SiOH \qquad (5)$$

Also, the trialkylsilanol produced by hydrolysis (eqn. 5) will tend to condense to the hexaalkyldisiloxane and water (eqn. 6). This precludes ebulliometric studies in the boiling silanol because the hydrolysis could not be controlled. Therefore the technique employed

$$2\ R_3SiOH \rightarrow R_3SiOSiR_3 + H_2O \qquad (6)$$

so successfully in studies on the metal oxide alkoxides was not available for the studies on the metal oxide trialkylsilyloxides. The hydrolysis of the metal trialkylsilyloxides was therefore usually carried out in dioxan solution and after the removal of solvent and other volatile products the residual metal oxide trialkylsilyloxide was characterized by analysis and the molecular weight determined cryoscopically in cyclohexane. Although the procedure was laborious and sometimes less accurate than the ebulliometric method used for the metal oxide alkoxides it had the advantage that the molecular weights referred to unsolvated species in hydrocarbon solution. Another difference between metal alkoxides and metal trialkylsilyloxides concerns the difference in steric effects between the trialkylsilyloxy group $R_3SiO$ and the corresponding tertiary carbinolate group $R_3CO$. It appears that the trialkylsilyloxy groups causes less steric hindrance to coordination polymerization because whereas titanium and zirconium tetra tert-butoxides are both monomeric the trimethylsilyloxides of titanium and zirconium have degrees of polymerization in benzene[3] of 1.21 and 2.05 respectively. This fact would be expected to have some bearing on the structural aspects of the metal oxide trialkylsilyloxides.

### *(i) Titanium oxide trimethylsilyloxides*

Studies on the hydrolysis of titanium tetra trimethylsilyloxide[14] in dioxan at room temperature gave some interesting results. It was found that the hydrolysis was slow (incomplete after one hour of reaction) and that the initially formed products disproportionated, slowly at room temperature, and rapidly at 160 °C, to give the volatile starting material and a non-volatile residue $TiO_x(OSiMe_3)_{(4-2x)}$ corresponding to a highly hydrolysed product ($x > 1.5$). Although the initial molecular ratio of water to $Ti(OSiMe_3)_4$ was varied from 0.1 to 2.5 the degree of hydrolysis ($x$) of the non-volatile residue only changed from 1.505 to 1.69. Products with $x = 1.505-1.645$ were soluble in cyclohexane and their molecular weights were determined and the number average degree of polymerization ($n$) was calculated. A linear relationship between $n^{-1}$ and $x$ was found: $n^{-1} = 1.028 - 0.604\,x$. Since the lowest polymer isolated was the octamer $Ti_8O_{12}(OSiMe_3)_8$ it was suggested that this had a special stability and the highly compact structure shown in Fig. 14 was considered to account for it. Further condensation by cross-linking between octamer units would lead to a polymer series A corresponding to $n^{-1} = 0.125-(x-1.5) = 1.625-x$. This was obviously at variance with the experimentally determined equation and it was considered that some condensation between octamers by double Ti–O–Ti bridges might have occurred giving a second polymer series B. This would require a line given by $n^{-1} = 0.125-0.5(x-1.5) = 0.875-0.5x$ which also did not agree with experiment. However, a mixture of 79.6% of the polymer series B with 20.4% of A gave excellent agreement with observed data. Actually quite reasonable agreement is also given for a mixture of 53.8% of the octamer series A and 46.2% of the $p_3q_4$ polymer series ($n^{-1} = 0.333 - 0.25x$) which was devised for titanium oxide ethoxides. The calculated slope of the $n^{-1}$ *versus* $x$ equation would be $-0.65$ compared with the observed value of $-0.604$ and although this discrepancy is extremely large it must be considered in the light of the coefficient of variation ($\sigma = \pm 6\%$) for the data which cover a very restricted range of $x$. However, a reason for doubting the presence of the $p_3q_4$ polymer series is that it should produce an infinite polymer at $x = 1.33$. This infinite polymer would surely be insoluble in cyclohexane whereas the products only became sparingly soluble when $x$ exceeded 1.65 and the octamer series A predicts an infinite polymer at $x = 1.625$. On the other hand the octamer series B predicts an infinite polymer at $x = 1.75$ so the proposed mixture of octamer series A and B could give soluble products for $x = 1.5$ to 1.65. Whether or not any of the $p_3q_4$ polymer series is present it is clearly necessary to include the octamer series A in order to approach the parameters of the experimentally determined line. The interesting feature of the octamer (Fig. 14) is that it contains 4-coordinated titanium and is purely a condensation polymer. It seems therefore that the silicon atom in the $TiOSiMe_3$ group has a profound effect on the structural chemistry of titanium oxide trimethylsilyloxides no doubt due to electronic factors because the steric effect of only one $Me_3SiO$ group per titanium in the octamer would be negligible. From the electronic viewpoint the silicon may withdraw electrons from the oxygen by $d\pi$-$p\pi$ bonding and thus lower the tendency of the oxygen in $TiOSiMe_3$ to coordinate to another titanium. This would guide the trimethylsilyloxy groups into terminal positions on the polymer but it still remains to be explained why the oxygen atoms in the Ti–O–Ti groups do not appear to coordinate to other titanium atoms.

### *(ii) Titanium oxide triethylsilyloxides*

The hydrolysis of $Ti(OSiEt_3)_4$ in dioxan was so slow that the experiments were carried out at 60 °C in order to produce titanium oxide triethylsilyloxides[17]. In the degree of hydrolysis range $x = 0$ to 0.5 the products were soluble in cyclohexane and gave a straight line: $n^{-1} = 0.996 - 0.993x$ corresponding to a $p_1q_1$ polymer series. The $p_1q_1$ series is based on the monomeric titanium unit with one Ti–O–Ti bridge between adjacent monomer units and there is no doubt that the steric hindrance of the triethylsilyloxy group plays a major part in preventing coordination polymerization. Moreover, it was considered that the products of hydrolysis would probably be hydrolysed much faster than $Ti(OSiEt_3)_4$ and that the distribution of polymers would be very extreme. For example it was thought that the initial polymers consisted of mixtures of predominantly the "unhydrolysed" $Ti(OSiEt_3)_4$ with small proportions of highly hydrolysed ($x \sim 1.0$) $p_1q_1$ polymers. When these initial polymers were heated (at 180 °C) *in vacuo* the volatile $Ti(OSiEt_3)_4$ was distilled out leaving insoluble residues which were much more highly hydrolysed ($x = 1.29$ to 1.70). Experiments are being carried out with the object of distilling out the $Ti(OSiEt_3)_4$ from the initial polymers at a much lower temperature under a high vacuum in order to avoid thermal disproportionation.

### *(iii) Zirconium oxide trimethylsilyloxides*

The hydrolysis of zirconium trimethylsilyloxide $Zr(OSiMe_3)_4$ gave soluble polymeric zirconium oxide trimethylsilyloxides $[ZrO_x(OSiMe_3)_{(4-2x)}]_n$ with $x = 0$ to 1.377[15]. From $x = 0$ to 0.948 a straight line relationship $n^{-1} = 0.480 - 0.381x$ was obtained corresponding to a mixture of predominantly (88.7%) the $p_3q_4$ polymer series and a small proportion (11.3%) of the octamer series A ($n^{-1} = 1.625 - x$) which was originally proposed for titanium oxide trimethylsilyloxides. For the higher values of $x$ (0.948 to 1.377) the observed values of $n$ deviated from the straight line in the sense that the $p_3q_4$ polymer series was diminishing in favour of the octamer series. The substantial amount of the $p_3q_4$ polymer series in the initial products ($x = 0$ to $0.948$) was not surprising in view of the polymeric nature of $Zr(OSiMe_3)_4$ which had a degree of polymerization of 2.05. Presumably steric hindrance by the trimethylsilyloxide groups prevents trimerization and the observed degree of polymerization may be due either to the presence of a dimeric compound or to equimolecular proportions of monomers and trimers. The latter would correspond to 75% of zirconium in the trimeric state $Zr_3(OSiMe_3)_{12}$ compared with 88.7% of zirconium in the $p_3q_4$ polymer series $Zr_{3(x+1)}O_{4x}(OSiMe_3)_{4(x+3)}$. The higher proportion in the $p_3q_4$ polymer series of zirconium oxide trimethylsilyloxides is not surprising because the steric hindrance to coordination polymerization should be less in the zirconium oxide trimethylsilyloxides due to smaller proportion of $Me_3SiO$ groups per zirconium compared with $Zr(OSiMe_3)_4$.

When the initial polymers ($x = 0$ to $0.948$) were heated at 150 °C *in vacuo* disproportionation occurred with formation of the volatile $Zr(OSiMe_3)_4$ and residual non-volatile polymers $[ZrO_x(OSiMe_3)_{(4-2x)}]_n$ ($x = 1.486$ to $1.63$). For values of $x < 1.62$ the polymers were soluble in cyclohexane and molecular weights were determined. The soluble residual polymers with $x$ in the range 1.486–1.541 gave a linear relationship between $n^{-1}$ and $x$, *viz*: $n^{-1} = 1.025 - 0.64x$. From the intercept $n^{-1} = 1.025$ at $x = 0$ it was calculated that 46.5% of the zirconium was in the $p_3q_4$ polymer series and 53.5% in the octamer A series. Such a mixture of polymer series would require a slope of $-0.65$ in excellent agreement with the observed slope of $-0.64$. In fact this equation is very similar to that found for the titanium oxide trimethylsilyloxide polymers (Table 5) and it lends support for the view that the titanium compounds consist of $p_3q_4$ and octamer A polymer series. The interesting feature of the zirconium oxide trimethylsilyloxide is the dramatic decrease in proportion of the $p_3q_4$ polymer series caused by thermal disproportionation. This is in fact quite reasonable from the structural viewpoint because the $p_3q_4$ structure alone is capable of facile formation of the volatile zirconium tetra trimethylsilyloxide. This can be seen by reference to the structurally similar titanium oxide ethoxide $Ti_6O_4(OEt)_{16}$ shown in Fig. 5. The "corner" metal

TABLE 5

METAL OXIDE TRIALKYLSILYLOXIDES

| *Trialkylsilyloxide* | $N_0$* | *Exptl. equation* | *% Polymer series* | *Slope of Equation* | |
|---|---|---|---|---|---|
| | | | | *Calc.* | *Exptl.* |
| $Ti(OSiMe_3)_4$ | 1.21 | $n^{-1} = 1.028 - 0.604x$ | (*i*) 20.4% Octamer A; 79.6% Octamer B<br>(*ii*) 53.8 Octamer A; 46.2% $p_3q_4$ | $-0.602$<br>$-0.653$ | $-0.604$ |
| $Ti(OSiEt_3)_4$ | 1.00 | $n^{-1} = 0.996 - 0.993x$ | 100% $p_1q_1$ | $-1.000$ | $-0.993$ |
| $Zr(OSiMe_3)_4$$^a$ | 2.05 | $n^{-1} = 0.480 - 0.381x$ | 11.3% Octamer A; 88.7% $p_3q_4$ | $-0.335$ | $-0.381$ |
| $Zr(OSiMe_3)_4$$^b$ | | $n^{-1} = 1.025 - 0.64x$ | 53.5% Octamer A; 46.5% $p_3q_4$ | $-0.65$ | $-0.64$ |
| $Ta(OSiMe_3)_5$ | 1.09 | $n^{-1} = 0.818 - 0.588x$ | 63.6% $p_1q_{1.5}$; 36.4% $p_2q_3$ | $-0.545$ | $-0.588$ |

$N_0$* = Initial degree of polymerization of $M(OSiR_3)_y$ in benzene.
$^a$ = Initial $ZrO_x(OSiMe_3)_{(4-2x)}$ polymers; $^b$ = Residual polymers.

atoms are each bonded to two terminal and two bridging ethoxide (or trimethylsilyloxide) groups and it is clear that these metals could be detached with all four ethoxide (or trimethylsilyloxide) groups by a slight electronic rearrangement involving dissociation of two coordinate bonds. The remaining portion of the polymer would link up with another fragment to produce a more highly hydrolysed species. In the case of the octamer A polymer which is based on $Zr_8O_{12}(OSiMe_3)_8$ which is analogous to the structure shown in Fig. 14 it is difficult to see how this species could eliminate a $Zr(OSiMe_3)_4$ molecule because no zirconium atom in the octamer unit has more than one trimethylsilyloxide group attached to it. Therefore it should be very difficult if not impossible for the octamer A polymer series to undergo disproportionation. Thus the action of heat on the initial polymers causes disproportionation of $p_3q_4$ polymers which leads to an increase in the relative amount of octamer A polymers left in the residual polymers.

### *(iv) Tantalum oxide trimethylsilyloxides*

When tantalum penta trimethylsilyloxide $Ta(OSiMe_3)_5$ was hydrolysed in a mixed solvent of dioxan-cyclohexane the products were found to contain coordinated dioxan and trimethylsilanol[16]. When heated at 120° *in vacuo* these initial polymers disproportionated leaving non-volatile residual polymers $[TaO_x(OSiMe_3)_{(5-2x)}]_n$ ($x$ = 0.469 to 1.202) which were soluble in cyclohexane. A linear plot of $n^{-1} = 0.818 - 0.588x$ was obtained and the intercept $n^{-1} = 0.818$ at $x = 0$ suggested that a mixture of $p_1$ and $p_2$ polymer series was present in the proportions of 63.6% tantalum in $p_1$ and 36.4% tantalum in $p_2$. Assuming that monomeric $Ta(OSiMe_3)_5$ has the trigonal bipyramidal structure there are various ways in which condensation polymers could arise giving either $p_1q_1$ or $p_1q_2$ polymer series. The dimeric species $Ta_2(OSiMe_3)_{10}$, which accounts for 16.5% of the tantalum in the "unhydrolysed" penta trimethylsilyloxide, would be expected to give the $p_2q_3$ polymer series analogous to the tantalum oxide alkoxides. Calculations showed that mixtures of $p_1q_1 + p_2q_3$ or $p_1q_2 + p_2q_3$ could not account for the parameters in the equation and it was necessary to assume that the $p_2q_3$ series was accompanied by approximately equal proportions of the $p_1q_1$ and $p_1q_2$ series to give reasonable agreement. It was therefore suggested that the $p_1$ polymers might be present as a hybrid $p_1q_{1.5}$ polymer series in which each tantalum has one Ta–O–Ta bridge with one neighbour and two Ta–O–Ta bridges with its other neighbour. An example of the $p_1q_{1.5}$ polymer series is shown in Fig. 15. A mixture

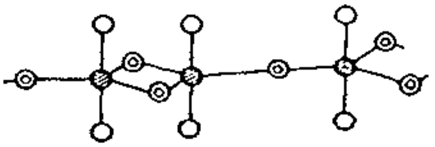


Fig. 15. $Ta_2O_3(OR)_4$ polymer series. ⊛ = Ta; ◉ = Oxygen in TaOTa; ○ = Oxygen in OR group.

of polymer series containing 63.6% of tantalum in the $p_1q_{1.5}$ series and 36.4% in the $p_3q_4$ series would require a slope of $-0.545$ compared with the experimentally determined value of $-0.588$. Best agreement is given by 36.4% $p_2q_3$ with 33.9% $p_1q_1$ and 29.7% $p_1q_2$ polymer series. It is noteworthy that tantalum penta trimethylsilyloxide has a degree of polymerization of 1.09 corresponding to only 12.9% tantalum in the dimeric form compared with 36.4% calculated to be present in the tantalum oxide trimethylsilyloxides. Once again this points to the operation of strong steric hindrance to the coordination polymerization of $Ta(OSiMe_3)_5$ compared with the small steric effects in the tantalum oxide trimethylsilyloxides which contain a smaller ratio of trimethylsilyloxy groups per tantalum atom.

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