687. *Organosilyloxy-derivatives of Metals. Part I. Alkylsilyloxy-derivatives of Titanium, Zirconium, Niobium, and Tantalum.**

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Compounds of the type $M(O{\cdot}SiMe_xEt_{3-x})_n$, $M(O{\cdot}SiMe_2Pr^n)_n$, and $M(O{\cdot}SiMe_2Pr^i)_n$ where $x = 3,2,1$, or 0, M = Ti, Zr, Nb, or Ta, and n is the valency of M, have been prepared by various methods. Their physico-chemical properties have been studied and are compared with the corresponding metal tertiary alkoxides. The organosilyloxy–metal compounds appear to be less susceptible to hydrolysis or thermal decomposition than the metal tertiary alkoxides.

TETRAKISTRIMETHYLSILYLOXYTITANIUM $Ti(O{\cdot}SiMe_3)_4$ was first reported by English and Sommer [1] in 1955. Although other authors [2,3,4,5] have since prepared this and other trialkylsilyloxytitanium compounds, the yields were often low and little was known about them when our systematic studies began. Furthermore we have extended these studies to cover other transition metals whose trialkylsilyloxy-derivatives are more difficult to prepare. Now we report the preparation of derivatives of titanium, zirconium, niobium, and tantalum together with the results of molecular-weight studies (ebulliometrically in benzene) and boiling points under reduced pressure.

Preparative Methods.—English and Sommer's [1] synthesis of tetrakistrimethylsilyloxytitanium involved the reaction between titanium tetrachloride and trimethylsilanol in benzene in the presence of ammonia, and they inferred that the low yield (18%) was caused by water produced in the acid-catalysed condensation of the silanol. Zeitler and Brown [2] obtained a better yield (56%) by the silanolysis of titanium tetra-n-butoxide in boiling toluene:

$$4Me_3Si{\cdot}OH + Ti(OBu)_4 \longrightarrow Ti(O{\cdot}SiMe_3)_4 + 4BuOH \quad . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

They isolated butoxytrimethylsilane among the products and it was thus clear that condensation of the silanol with the butyl alcohol liberated by silanolysis also produced water which hydrolysed the titanium compounds. This behaviour confirmed our independent experiences with the trimethylsilanolysis of titanium or zirconium isopropoxides and it was clear that good yields of these trimethylsilyloxy-derivatives would only result under conditions which suppressed the condensation reactions of the silanol. Obviously the concentrations of silanol and liberated alcohol (in the silanolysis) must be minimised. By

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[1] English and Sommer, *J. Amer. Chem. Soc*, 1955, **77**, 170.

[2] Zeitler and Brown, *ibid.*, 1957, **79**, 170.

[3] Dolgov and Orlov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1957, 1395; *Doklady. Akad. Nauk S.S.S.R.*, 1957, **117**, 617.

[4] Andrianov, Zhdanov, Kurasheva, and Dvlova, *Doklady Akad. Nauk S.S.S.R.*, 1957, **112**, 1050.

[5] Bradley and Thomas, *Chem. and Ind.*, 1958, 17.

slow addition of the silanol in benzene to a boiling solution of the metal alkoxide in benzene, and constant removal of the liberated alcohol by azeotropic distillation, the titanium compound was quantitatively produced and the zirconium compound obtained in 70% yield. The pentakistrimethylsilyloxy-derivatives of niobium and tantalum were similarly obtained in 50% yield, whilst with the higher silanols, which are less readily condensed, practically quantitative yields were obtained with the four metals. Further evidence of the condensation of trimethylsilanol was obtained during attempts to reverse the silanolysis (1) by addition of n-butyl alcohol to tetrakistrimethylsilyloxytitanium, whereupon water appeared with the liberated silanol and the yield of titanium butoxide was low. It was interesting that silanolysis of trimethylsilyloxy-derivatives in boiling hexamethyldisiloxane does not cause condensation, and quantitative yields of trialkylsilyloxy-derivatives are afforded by this new method:

$$M(O{\cdot}SiMe_3)_n + nR_3Si{\cdot}OH \longrightarrow M(O{\cdot}SiR_3)_n + nMe_3Si{\cdot}OH \quad . \ . \ . \ . \ . \ . \ . \quad (2)$$

In a preliminary communication [6] we have also reported another new general method of preparation based on trans-esterification: condensation is eliminated by using the trialkylsilyl acetate in place of the silanol and the reaction is conducted in boiling cyclohexane with which isopropyl or ethyl acetate forms minimum-boiling azeotropes. A quantitative yield of tetrakistrimethylsilyloxytitanium was thus obtained:

$$Ti(OR)_4 + 4Me_3Si{\cdot}OAc \longrightarrow Ti(O{\cdot}SiMe)_4 + 4ROAc \quad . \ . \ . \ . \ . \ . \ . \quad (3)$$

The corresponding zirconium and tantalum compounds were obtained in 56% and 75% yields respectively. Even in this method it is important to add the trimethylsilyl acetate in cyclohexane slowly to the metal alkoxide because the silyl acetate appears to acetylate the silyloxy–metal compound when present in excess. With the higher alkylsilyl acetates two features were apparent: first, the rate of reaction (3) decreases with increase in size of the organosilyl group and secondly the tendency to cause acetylation also decreases, and it seems probable that steric effects are playing an important rôle. An interesting feature of reaction (3) is its apparent irreversibility. Thus tetrakistrimethylsilyloxytitanium and n-butyl acetate were heated in boiling toluene for 6 hr. but trimethylsilyl acetate could not be detected. On the other hand, metal alkoxides undergo reversible trans-esterification with alkyl acetates.

Properties of Alkylsilyloxy–Metal Compounds.—The alkylsilyloxy-compounds were colourless liquids or white solids which could be distilled or sublimed under reduced pressure. In Table 1 are presented the melting points, boiling points, and degrees of polymerisation (*n*) for the ethylmethylsilyloxy- and isomeric dimethylpropylsilyloxy-titanium, -zirconium and -tantalum compounds. The melting points of the ethylmethylsilyloxy-series show some interesting trends. For titanium all except the triethylsilyloxy-compound are liquids, and for zirconium all except the triethylsilyloxy-compound are solids. For zirconium the melting point decreases steadily as methyl groups are replaced by ethyl but for tantalum the reverse occurs. Similarly, with zirconium the dimethyl-n-propylsilyloxy-compound is a solid and the isopropyldimethylsilyloxy-compound is a

TABLE 1.

	Ti			Zr			Ta		
Alkylsilyl oxide	M. p.	B. p./mm.	*n*	M. p.	B. p./mm.	*n*	M. p.	B. p./mm.	*n*
Me_3SiO	L	60°/0·1	1·21	152°	135°/0·1 *	2·05	80°	84°/0·05	1·08
Me_2EtSiO	L	86/0·1	1·00	105	105/0·1	1·20	135	135/0·1 *	0·98
$MeEt_2SiO$	L	120/0·1	0·99	30	120/0·1	1·05	180	170/0·1 *	1·00
Et_3SiO	110°	150/0·1	1·00	L	147/0·1	0·98	210	210/0·1 *	0·98
Pr^nMe_2SiO	L	112/0·2	0·99	60	103/0·05	1·11	L	170/0·1	1·00
Pr^iMe_2SiO	L	115/0·2	1·00	L	110/0·1	1·01	180	165/0·1 *	1·02

L = Liquid. * Sublimes.

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[6] Bradley and Thomas, *Chem and Ind.*, 1958, 1231.

liquid but for tantalum the opposite is the case. It would be unwise to infer any structural implications from these data because some of the compounds are polymeric, but the extra alkylsilyloxy-group around the tantalum (cf. zirconium) clearly has important structural consequences. The most surprising feature is that in the triethylsilyloxy-compounds the titanium derivative has a fairly high melting point whilst the zirconium derivative is liquid, although both compounds are monomeric and very similar in volatility. Molecular-weight determinations have revealed some interesting facts. For example, among the titanium compounds the trimethylsilyloxy-derivative shows a significant degree of polymerisation whereas all of the others are monomeric. This result is particularly interesting because titanium tetra-t-butoxide is monomeric. In the zirconium compounds polymerisation is even greater and more extensive and it decreases steadily as methyl groups are replaced by ethyl, suggesting that steric effects operate. The latter point is further supported by the behaviour of the isomer dimethylpropylsilyloxyzirconium as compared with that of the isomeric diethylmethylsilyloxy-derivative. Even in the trimethylsilyloxytantalum there is a small but significant degree of polymerisation whereas tantalum penta-t-butoxide is monomeric. This contrast in structural behaviour between trialkylsilyloxy-derivatives and the corresponding tertiary alkoxides demands explanation. Extensive studies on the metal alkoxides [7] showed that the decrease in degree of polymerisation with increased branching of the alkyl groups was mainly due to the steric effect of the alkyl groups and this must be a fundamental structural phenomenon which should operate also in the trialkylsilyloxy-derivatives. However, the replacement of the carbinol carbon atoms of the tertiary alkoxide by silicon atoms must cause some electronic disturbance, especially as partial double bonding involving donation of electrons from a p_π orbital of oxygen to a vacant d_π orbital of silicon may occur. The latter effect will be partly offset by the greater electronegativity of carbon compared with silicon but the fact that trimethylsilanol is more acidic than t-butyl alcohol suggests that the trimethylsilyloxy-group is more electron-attracting than the t-butoxy-group. It seems reasonable to suppose that the strength of intermolecular bonds involving metal and oxygen in these types of compound will increase with the electron density on the donor oxygen. This being accepted, it follows that from the electronic point of view a trialkylsilyloxy–metal compound should form less stable polymers than the corresponding metal t-alkoxide because of the reduced electron density on the oxygen in $R_3Si^{-}=^{+}O-$ compared with that of the oxygen in $R_3C{\cdot}O{\cdot}$. The experimental results thus indicate that steric effects must be the cause of the higher degree of polymerisation of trialkylsilyloxy-zirconium compared with the corresponding zirconium t-alkoxides. This is interesting because the silicon atoms will provide better shielding of the metal than the smaller carbinol carbon atoms. The smaller net shielding ability of the trialkylsilyloxy-group compared with the corresponding t-alkoxy-group may be caused by two factors. First, the Si–O bond's being longer than the C–O causes the alkyl groups in $R_3Si{\cdot}O{\cdot}M$ to be slightly further from the metal than in $R_3C{\cdot}O{\cdot}M$ and our studies on the metal alkoxides [7] have shown that the nearer that chain branching is to the metal the more effective is the shielding given by the alkyl group. Secondly, the partial double bonding $^{-}Si{=}O^{+}$ may result in the SiOM bond angle's being larger than $\angle$COM with consequent decrease in shielding power of the R_3SiO group. In addition to the data in Table 1 we have other evidence which suggests that the steric effects of R_3SiO groups are smaller than for R_3CO groups. In the alcoholysis of niobium or tantalum primary alkoxides with secondary or tertiary alcohols it appears that steric factors cause difficulties in replacing the fifth alkoxide group and compounds of the type $Ta(OR)(OR')_4$, where $R =$ primary and $R' =$ secondary or tertiary alkyl, can be isolated.[8] However, we found no difficulty in replacing all of the ethoxy-groups in niobium or tantalum pentaethoxide with the trialkylsilyloxy-groups.

The importance of polymerisation in the lower trialkylsilyloxy-derivatives of titanium

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[7] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 2027, and later papers in this series.

[8] Bradley, Chatterjee, Chakravarti, Wardlaw, and Whitley, *J.*, 1958, 99.

and zirconium is also apparent when their volatilities (Table 1) are compared together and with the corresponding t-alkoxides. Thus $Zr(O{\cdot}SiMe_3)_4$ is considerably less volatile than $Ti(O{\cdot}SiMe_3)_4$ which is also a little less volatile than the monomeric $Ti(O{\cdot}CMe_3)_4$ (b. p. 54°/0·1 mm.). The monomeric trialkylsilyloxy-derivatives of titanium and zirconium have very similar volatilities with a suggestion that the zirconium compounds are slightly the more volatile. Also the monomeric organosilyloxy-compounds appear to be slightly more volatile than the corresponding t-alkoxides and these facts are of importance in connection with the fundamental effect of mass on volatility.[9] This aspect of the work will be discussed later when more extensive vapour-pressure measurements are available.

Attempts to prepare niobium penta-t-alkoxides were unsuccessful owing to the tendency of these compounds to form the oxyalkoxides $Nb_2O(OR)_8$, and it was believed that the decomposition was promoted by the electron-releasing tendency of the t-alkyl groups.[10] In this work we obtained pentakistrimethylsilyloxyniobium which was distilled without decomposition at 120°/0·1 mm. and niobium pentakisdiethylmethylsilyloxyniobium which was sublimed at 140°/10^{-4} mm. There is little doubt that other organosilyloxyniobium compounds could also be obtained and their higher stability than of the t-alkoxides is consistent with the suggestion that the electron-releasing tendency of the trialkylsilyl group is counteracted by the d_π–p_π bonding between silicon and oxygen.

The organosilyloxy-derivatives of titanium, zirconium, niobium, and tantalum are noticeably less susceptible to hydrolysis and have greater thermal stability than the corresponding metal t-alkoxides. The resistance to hydrolysis appears to be connected with the water-repellent properties of the organosilicon groups whilst the high thermal stability is undoubtedly due to the fact that tertiary alcohols undergo thermolytic dehydration to give 1 mole of water per mole of alcohol whereas the silanols on condensation give only 1 mole of water per *two* moles of silanol (the thermal decomposition of the metal t-alkoxide being due to a hydrolytic chain reaction [11]).

EXPERIMENTAL

Preparation of Metal Alkoxides.—The alkoxides of titanium,[7] zirconium,[7] niobium,[12] and tantalum [13] were prepared by the literature methods and were freshly distilled under reduced pressure immediately before use.

Preparation of the Silanols.—Except for trimethylsilanol, the organosilanols were obtained by alkaline hydrolysis of the appropriate organosilyl chloride which was prepared from commercial alkylethoxysilane or ethyl orthosilicate by the following general reaction sequence:

$$Me_nSi(OEt)_{4-n} \xrightarrow{RMgBr} Me_nR_{3-n}Si(OEt) \xrightarrow{HCl,\ aq.} Me_nR_{3-n}Si{\cdot}O{\cdot}SiR_{3-n}Me_n \xrightarrow[NH_4Cl]{H_2SO_4\ conc.} Me_nR_{3-n}SiCl$$

Trimethylsilanol was obtained by hydrolysis of trimethylfluorosilane by the method of Sommer *et al.*[14] The organosilanols, in ether, were dried (K_2CO_3), the ether was evaporated off under reduced pressure, and the silanol then distilled. The following b. p.s were recorded: $Me_3Si{\cdot}OH$, 98·5—99·0°/763 mm.; $Me_2EtSi{\cdot}OH$, 119·5—120°/774 mm.; $MeEt_2Si{\cdot}OH$, 137·5—138·5°/758 mm.; $Et_3Si{\cdot}OH$, 167°/763 mm.; $Me_2Pr^nSi{\cdot}OH$, 137—138·5°/740 mm.; $Me_2Pr^iSi{\cdot}OH$, 131—132°/746 mm. For work involving the silanols the apparatus was rinsed first with alcoholic sodium hydroxide solution, and then distilled water, before being dried at 140°. The alkaline rinse proved an effective precaution against the ready acid-catalysed condensation of the silanol.

Preparation of Organosilyl Acetates.—Since the organosilyl chlorides were prepared as intermediates for the silanols they were conveniently used for preparing organosilyl acetates. Trimethylsilyl acetate (b. p. 102·5—103°/740 mm.) was obtained by the method of Schuyten *et al.*[15] by reaction between anhydrous sodium acetate and trimethylchlorosilane in ether

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[9] Bradley, *Nature*, 1954, **174**, 323.

[10] Bradley, Chakravarti, and Wardlaw, *J.*, 1956, 4439.

[11] Bradley and Faktor, *J. Appl. Chem.*, in the press; *Trans. Faraday Soc.*, in the press.

[12] Bradley, Chakravarti, and Wardlaw, *J.*, 1956, 2381.

[13] Bradley, Whitley, and Wardlaw, *J.*, 1955, 726.

[14] Sommer, Pietrusza, and Whitmore, *J. Amer. Chem. Soc.*, 1946, **68**, 2282.

[15] Schuyten, Weaver, and Reid, *ibid.*, 1947, **69**, 2110.

(Found: OAc, 44·5. Calc. for $CH_3{\cdot}CO_2SiMe_3$: OAc, 44·7%). This procedure was not suitable for preparing the higher organosilyl acetates which were obtained as follows: The chlorosilane was heated at just below reflux temperature with excess of sodium acetate for 3 hr. The liquid obtained by decantation was fractionally distilled to give the organosilyl acetate. The following results were obtained: $CH_3{\cdot}CO_2SiMe_2Et$, b. p. 127—128°/746 mm. (Found: OAc, 40·1. Calc., 40·3%). $CH_3{\cdot}CO_2SiMeEt_2$, b. p. 150—151·5°/732 mm. (Found: OAc, 36·7. Calc., 36·9%). $CH_3{\cdot}CO_2SiEt_3$, b. p. 168·5—169·0°/765 mm. (Found: OAc, 33·8. Calc., 33·9%). Although the organosilyl acetates are readily hydrolysed it was possible to store them in stoppered bottles. The acetate determinations were carried out by titration of the hydrolysed sample with standard alkali after allowing 10 min. for completion of the hydrolysis.

Analytical Methods.—(i) *Metal.* The sample (*ca.* 0·3 g.) was weighed into a platinum crucible and dissolved in ethyl alcohol (2 c.c.). Ammonia solution (*d* 0·88, 3 c.c.) was added and the mixture cautiously evaporated to dryness by using an infrared lamp. This procedure removed the silicon as volatile organosilanol and left the metal as the hydrated oxide which was then ignited and weighed as oxide. The zirconium analyses were not corrected for the hafnium present (0·2—2·0%) but the error is not likely to exceed 0·5% of the zirconium figure.

(ii) *Silicon.* The sample (*ca.* 0·3 g.) was weighed into a beaker (400 c.c.) containing sulphuric acid (*d* 1·84, 30 c.c.) and ammonium nitrate (5 g.) and ammonium sulphate (5 g.) were then added. The mixture was heated, gently at first to convert the organosilicon groups into silica, then more strongly to evaporate off the excess of nitric acid, and finally at about the b. p. for 2 hr. to render the silica insoluble. The cooled contents of the beaker were poured into water (300 c.c.) and the silica filtered off on paper (Whatman No. 41), washed well with water, and finally ignited and weighed. With the niobium and tantalum compounds the silica was always contaminated with traces of metal oxide and the true silica content was obtained by difference after the removal of silicon as the tetrafluoride by treatment with hydrofluoric acid (10%, 4 c.c.) and a few drops of sulphuric acid, followed by evaporation under the infrared lamp and ignition of the residue.

(iii) *Alkoxide.* Ethoxide or isopropoxide was determined by the chromic acid method of Bradley *et al.*[16] which was unaffected by the presence of the organosilyloxy-groups. This method was used to confirm that all the alkoxide had been replaced by organosilyloxy-groups.

Silanolysis of Metal Alkoxides.—When titanium isopropoxide and trimethylsilanol were refluxed in benzene under a fractionating column the production of water was indicated by the appearance of some ternary azeotrope of benzene–water–isopropyl alcohol. After the removal of the remaining isopropyl alcohol as the binary azeotrope (benzene), and then the solvent, some tetrakistrimethylsilyloxytitanium [47% yield; b. p. 69°/0·5 mm. Found: Ti, 11·9. Calc. for $Ti(O{\cdot}SiMe_3)_4$: Ti, 11·8%] was distilled out. The presence of water in the first distillate and the low yield indicated condensations of the reactive silanol. Similarly when zirconium isopropoxide was treated with trimethylsilanol as above, a white *solid* [Found: Zr, 23·0. $Zr(O{\cdot}SiMe_3)_4$ requires Zr, 20·4%], which could not be sublimed up to 150°/0·1 mm., was obtained and was evidently a hydrolysis product. In preparing organosilyloxy-metal derivatives the silanolysis was carried out as follows: The silanol (10% excess over theoretical quantity) in benzene (*ca.* 15 c.c.) was added during several hours to a freshly distilled sample of the metal alkoxide refluxing in benzene (*ca.* 70 c.c.) under a fractionating column to remove the liberated alcohol as it was formed as the binary azeotrope with benzene. By this means the concentrations of silanol and alcohol were kept low and condensation of the silanol avoided. After removal of the alcohol the solvent and excess of silanol were evaporated off under reduced pressure and the metal organosilyloxide finally distilled or sublimed out *in vacuo*. Since essentially the same technique was used in each preparation we present the experimental details in abbreviated form in Table 2.

The yields in Table 2 are based on the pure distillate and it is noteworthy that whereas all of the titanium compounds are obtained quantitatively, for zirconium, niobium, and tantalum the yield increases steadily as the tendency of the silanol to condense decreases. It is possible that still higher yields of the lower alkylsilyloxy-compounds could be obtained with a further modification of technique whereby solutions of silanol and of metal alkoxide were each added slowly to the refluxing solvent. By this means the concentration of metal alkoxide would also be kept low and the metal-alkoxide catalysed condensation of the silanol avoided. The lower yield of zirconium trimethylsilyloxide than of the titanium compound is probably due to the

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[16] Bradley, Halim, and Wardlaw, *J.*, 1950, 3450.

TABLE 2.

Product	Silanol taken (g.)	Alkoxide taken (g.)	Yield (g.)	Yield (%)	Analyses Found (%) M	Analyses Found (%) Si	Analyses Calc. (%) M	Analyses Calc. (%) Si
$Ti(O{\cdot}SiMe_3)_4$	6·90	5·12[a]	7·29	100	11·7	—	11·8	—
$Ti(O{\cdot}SiMe_2Et)_4$	6·80	4·27[a]	6·49	94	10·4	24·5	10·4	24·4
$Ti(O{\cdot}SiMeEt_2)_4$	8·00	4·02[a]	7·17	98	9·31	21·7	9·27	21·7
$Ti(O{\cdot}SiEt_3)_4$	9·50	4·80[a]	9·02	94	8·40	19·6	8·36	19·6
$Ti(O{\cdot}SiMe_2Pr^n)_4$	19·8	10·2[a]	18·3	99	9·29	21·6	9·27	21·7
$Ti(O{\cdot}SiMe_2Pr^n)_4$	19·5	10·1[a]	18·0	98	9·20	21·7	,,	,,
$Zr(O{\cdot}SiMe_3)_4$	7·90	5·93[b]	5·93	73	20·4	—	20·4	—
$Zr(O{\cdot}SiMe_2Et)_4$	18·5	13·2[c]	14·3	79	18·2	22·1	18·1	22·3
$Zr(O{\cdot}SiMeEt_2)_4$	10·5	5·98[b]	9·58	95	16·5	20·0	16·3	20·0
$Zr(O{\cdot}SiEt_3)_4$	11·5	6·69[b]	12·4	99	14·9	18·2	14·8	18·2
$Zr(O{\cdot}SiMe_2Pr^n)_4$	21·0	14·4[c]	16·9	81	16·2	20·0	16·3	20·0
$Zr(O{\cdot}SiMe_2Pr^i)_4$	11·0	7·30[c]	10·1	91	16·2	20·1	,,	,,
$Ta(O{\cdot}SiMe_3)_5$	4·70	4·15[d]	3·27	48	28·9	22·4	28·9	22·4
$Ta(O{\cdot}SiMe_2Et)_5$	6·50	4·64[d]	6·55	82	26·0	20·3	25·9	20·1
$Ta(O{\cdot}SiMeEt_2)_5$	8·30	5·37[d]	8·70	86	23·6	18·2	23·6	18·3
$Ta(O{\cdot}SiEt_3)_5$	9·00	4·09[d]	8·23	96	21·6	16·7	21·6	16·8
$Ta(O{\cdot}SiMe_2Pr^n)_5$	5·00	2·51[d]	4·30	91	23·6	18·4	23·6	18·3
$Ta(O{\cdot}SiMe_2Pr^i)_5$	9·00	5·62[d]	9·95	95	23·8	18·2	,,	,,
$Nb(O{\cdot}SiMe_3)_5$	2·62	1·81[e]	1·57	54	17·4	—	17·2	—
$Nb(O{\cdot}SiMeEt_2)_5$	4·40	2·13[e]	4·09	90	13·7	20·4	$13{\cdot}6_5$	$20{\cdot}6_5$

[a] $Ti(OPr^i)_4$, [b] $Zr(OPr^i)_4$, [c] $Zr(OBu^t)_4$, [d] $Ta(OEt)_5$, [e] $Nb(OEt)_5$.

fact that zirconium alkoxides are stronger "Lewis-acids" than titanium alkoxides and also because the zirconium compounds are more readily hydrolysed.

Silanolysis of Metal Trimethylsilyloxides.—These reactions were carried out similarly to silanolyses of the metal alkoxide except that hexamethyldisiloxane was used as solvent because it forms a convenient minimum-boiling azeotrope with trimethylsilanol. The higher silanol in hexamethyldisiloxane (*ca.* 15 c.c.) was added slowly to the boiling solution of metal trimethylsilyloxide in hexamethyldisiloxane (*ca.* 120 c.c.) and the liberated trimethylsilanol removed by fractionation. The higher alkylsilyloxy-metal compound was finally isolated by vacuum distillation. Details are in Table 3.

TABLE 3.

Product	Silanol taken (g.)	$M(O{\cdot}SiMe_3)_x$ (g.)	Yield of product (g.)	Yield of product (%)	Found (%) M	Found (%) Si
$Ti(O{\cdot}SiMe_2Et)_4$	10·0	6·90	7·85	100	10·4	24·2
$Ti(O{\cdot}SiMeEt_2)_4$	8·40	6·72	7·71	90	9·27	21·6
$Ti(O{\cdot}SiEt_3)_4$	6·00	4·18	5·57	94	8·37	19·5
$Zr(O{\cdot}SiMe_2Et)_4$	6·75	4·77	5·20	97	18·2	22·4
$Zr(O{\cdot}SiEt_3)_4$	5·30	4·22	5·28	91	14·9	18·2
$Ta(O{\cdot}SiMe_2Et)_5$	2·00	1·72	1·80	94	26·0	20·4
$Ta(O{\cdot}SiMeEt_2)_5$	1·70	1·59	1·90	98	23·6	18·2
$Ta(O{\cdot}SiEt_3)_5$	3·25	3·02	3·55	88	21·6	16·8

It is noteworthy that these reactions are all practically quantitative in spite of the fact that the reactive trimethylsilanol is liberated in each case and it appears that the metal alkylsilyloxides do not catalyse its condensation.

Reaction between Tetrakistrimethylsilyloxytitanium and n-Butyl Alcohol.—To the titanium compound (5·45 g.) in boiling toluene (70 c.c.) was slowly added a solution of n-butyl alcohol (8·0 g.) in toluene (20 c.c.) and the mixture was fractionated. Water was detected in the distillate, and after about 3 hr. pure solvent was collected. Removal of excess of solvent under reduced pressure left a liquid (3·40 g.) which was free from silicon. A sample (3·00 g.) heated under reduced pressure gave some *titanium tetrabutoxide* [1·00 g. Found: Ti, 14·3. $Ti(OBu)_4$ requires Ti, 14·1%]. The presence of water in the volatile products and the low yield of titanium butoxide confirmed that the silanol undergoes condensation in the presence of the metal alkoxide and the butyl alcohol.

Reactions involving Metal Alkoxides and Organosilyl Acetates.—(i) *Titanium isopropoxide and trimethylsilyl acetate.* Titanium isopropoxide (2·12 g.) and trimethylsilyl acetate (10·4 g.) were refluxed under a fractionating column and during the first 15 min. isopropyl acetate was distilled out. After about 35 min. the liberation of isopropyl acetate was practically complete and a solid separated. The fine white powder (2·20 g.) remaining after the removal of excess of trimethylsilyl acetate contained no isopropoxide but a large amount of acetate (Found: Ti, 24·0; OAc, 36·3; Si, 3·7%).

(ii) *Tetrakistrimethylsilyloxytitanium and trimethylsilyl acetate.* From the foregoing reaction it appeared that although a trans-esterification occurs initially, the metal trimethylsilyloxide becomes acetylated by the excess of trimethylsilyl acetate. This was proved when tetrakistrimethylsilyloxytitanium (5·0 g.) was refluxed with trimethylsilyl acetate (10·0 g.) under similar conditions to the previous experiment. Solid was slowly precipitated and had a composition similar to the product of the previous reaction (Found: Ti, 23·7; OAc, 42·7; Si, 1·8%).

(iii) *Preparation of metal organosilyloxides.* The foregoing acetylation side-reactions were avoided by using only the theoretical quantity of organosilyl acetate and conducting the reactions in cyclohexane which forms minimum-boiling azeotropes with either ethyl or isopropyl acetate. Trimethylsilyl acetate was added slowly as a solution in cyclohexane (*ca.* 20 c.c.) to the metal alkoxide in cyclohexane (*ca.* 120 c.c.), and the alkyl acetate fractionated out as it formed. With the higher alkylsilyl acetates the trans-esterification is much slower and acetylation less important; hence the whole of the reactants were added together at the beginning of the reaction. In general the trans-esterifications required much longer than the corresponding silanolyses for completion. The products were isolated in the usual way and details are in Table 4.

The reversibility of the trans-esterification was explored by heating tetrakistrimethylsilyloxytitanium (2·57 g.) and n-butyl acetate (3·0 g.) in toluene (70 c.c.) under a fractionating column. Toluene was the sole constituent of the distillate during 6 hr. and the failure to produce trimethylsilyl acetate and titanium butoxide was confirmed when the solvent and n-butyl acetate were distilled off leaving the original titanium compound (Found: Ti, 11·8%).

Molecular-weight Determinations.—Some measurements were carried out in boiling benzene in an all-glass ebulliometer incorporating a differential water thermometer of the type previously described.[17] The internal calibration method [18] with pure fluorene was used with 15—16 g. of benzene per experiment. Although approximately fivefold ranges of concentration were covered, the apparent molecular weight was independent of concentration. Results are in Table 5 (*m* is the weight of solute).

TABLE 4.

Product	Acetate taken (g.)	Alkoxide taken (g.)	Yield (g.)	Yield (%)	Reaction time (hr.)	Found, % M	Found, % Si
$Ti(O{\cdot}SiMe_3)_4$	56·0	29·4[a]	39·7	95	10	12·0	—
$Ti(O{\cdot}SiMe_2Et)_4$	18·0	8·37[a]	13·1	97	9	10·4	24·0
$Ti(O{\cdot}SiMeEt_2)_4$	18·5	7·67[a]	13·3	96	35	9·37	21·7
$Ti(O{\cdot}SiEt_3)_4$	12·0	3·90[a]	7·75	93	132	8·40	19·5
$Zr(O{\cdot}SiMe_3)_4$	26·0	15·2[b]	11·5	56	28	20·4	—
$Zr(O{\cdot}SiMe_2Et)_4$	11·6	6·20[b]	7·64	80	10	18·2	22·1
$Zr(O{\cdot}SiMeEt_2)_4$	13·0	5·79[b]	9·11	92	18	16·4	20·1
$Zr(O{\cdot}SiEt_3)_4$	9·00	2·81[b]	4·75	90	132	14·9	18·2
$Ta(O{\cdot}SiMe_3)_5$	19·5	11·8[d]	13·4	74	18	28·9	22·2
$Ta(O{\cdot}SiMe_2Et)_5$	17·0	3·68[d]	5·56	88	8	26·0	20·1
$Ta(O{\cdot}SiMeEt_2)_5$	10·0	4·40[d]	5·97	72	30	23·6	18·4

a, b, d As in Table 2.

TABLE 5.

Metal organosilyloxide			Fluorene		*M*	
Compound	Range in *m* (g.)	$\Delta T/m$(°/g.)	Range in *m* (g.)	$\Delta T/m$(°/g.)	Found	Calc.
$Ti(O{\cdot}SiMe_3)_4$	0·0523—0·2720	0·357	0·0270—0·1200	1·050	488	404·9
$Ti(O{\cdot}SiMeEt_2)_4$ ...	0·0810—0·3770	0·346	0·0460—0·1520	1·059	508	516·8
$Ti(O{\cdot}SiEt_3)_4$	0·2660—0·6850	0·333	0·2054—0·3711	1·139	569	572·9
$Zr(O{\cdot}SiEt_3)_4$	0·0840—0·4100	0·279	0·0480—0·1440	1·012	602	616·2

The majority of measurements were made with a new all-glass ebulliometer incorporating a multi-junction differential thermocouple constructed by H. Holloway (to be described in a

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[17] Bradley, Gaze, and Wardlaw, *J.*, 1955, 3977.

[18] Bradley, Whitley, and Wardlaw, *J.*, 1956, 5.

later communication). The internal calibration method was used with either fluorene or diphenyl and the results are in Table 6. About 16—18 g. of benzene were used per experiment.

One difficulty experienced in this work was the tendency of boiling benzene solutions of metal organosilyloxides to froth. This was originally ascribed to the presence of traces of silicone vacuum grease acquired during vacuum distillation of the metal compound immediately before the ebullioscopic measurements. Nevertheless, in spite of extreme precautions taken to avoid contamination by Silicone the frothing remained and it is concluded that the metal organosilyloxides are surface-active in benzene. By improving the thermal insulation of the apparatus and using low boil-up rates the degree of frothing was not allowed to impair the accuracy of the measurements. The results are very probably accurate to within 5% and probably to within 2%, so that the small degrees of polymerisation found with $\mathrm{Ti(O{\cdot}SiMe_3)_4}$, $\mathrm{Zr(O{\cdot}SiMe_2Et)_4}$, $\mathrm{Zr(O{\cdot}SiMe_2Pr^n)_4}$, $\mathrm{Ta(O{\cdot}SiMe_3)_5}$, and possibly with $\mathrm{Zr(O{\cdot}SiMeEt_2)_4}$ are significant.

TABLE 6.

Metal organosilyloxide			Calibrant		*M*	
Compound	Range in *m* (g.)	Δ*T*/*m* *	Range in *m* (g.)	Δ*T*/*m* *	Found	Calc.
$\mathrm{Ti(O{\cdot}SiMe_2Et)_4}$	0·2340—1·155	296	0·0961—0·4682 †	889	462	460·7
$\mathrm{Ti(O{\cdot}SiMe_2Pr^i)_4}$	0·1250—0·6159	165	0·0320—0·1204 ‡	511	516	516·8
$\mathrm{Ti(O{\cdot}SiMe_2Pr^n)_4}$	0·0658—0·5854	166	0·0148—0·1017 ‡	510	511	516·8
$\mathrm{Zr(O{\cdot}SiMe_3)_4}$	0·1190—1·442	126	0·1823—0·4201 †	750	916	447·9
$\mathrm{Zr(O{\cdot}SiMe_2Et)_4}$	0·1776—0·5717	148	0·0321—0·0994 ‡	536	602	504·0
$\mathrm{Zr(O{\cdot}SiMe_2Pr^i)_4}$	0·1127—0·6073	151	0·0101—0·1238 ‡	516	568	560·1
$\mathrm{Zr(O{\cdot}SiMe_2Pr^n)_4}$	0·0763—0·5943	140·5	0·0472—0·1208 ‡	525	621	560·1
$\mathrm{Zr(O{\cdot}SiMeEt_2)_4}$	0·0977—0·6224	146·5	0·0225—0·1336 ‡	517	586	560·1
$\mathrm{Ta(O{\cdot}SiMe_3)_5}$	0·2037—0·8597	117	0·0517—0·1736 ‡	478	678	626·7
$\mathrm{Ta(O{\cdot}SiMe_2Et)_5}$	0·2520—1·200	181	0·0832—0·1960 †	800	681	696·8
$\mathrm{Ta(O{\cdot}SiMe_2Pr^i)_5}$	0·1702—0·9947	114·5	0·0200—0·0794 ‡	540	783	767·0
$\mathrm{Ta(O{\cdot}SiMe_2Pr^n)_5}$	0·1107—0·7643	115	0·0351—0·1325 ‡	530	765	767·0
$\mathrm{Ta(O{\cdot}SiMeEt_2)_5}$	0·1178—0·3440	175·5	0·0240—0·1908 †	870	763	767·0
$\mathrm{Ta(O{\cdot}SiEt_3)_5}$	0·1371—0·5709	202	0·0820—0·3503 †	1080	824	837·1

* In arbitary e.m.f. units/g.; † diphenyl; ‡ fluorene.

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