237. *Structural Chemistry of the Alkoxides. Part V.* Isomeric Butoxides and Pentyloxides of Quinquevalent Tantalum.*

By D. C. BRADLEY, W. WARDLAW, and (MISS) A. WHITLEY.

The isomeric butoxides $Ta(O{\cdot}C_4H_9)_5$ and the isomeric pentyloxides $Ta(O{\cdot}C_5H_{11})_5$ of tantalum have been prepared by various methods. Boiling points under reduced pressure, and molecular weights, were determined and the results are discussed in terms of the steric theory for metal alkoxides.

WE have already reported [1] that tantalum penta-*n*-alkoxides, $Ta(O{\cdot}C_nH_{2n+1})_5$ where $n = 1$—4, are dimeric in boiling benzene. In other solvents, such as toluene, pyridine, acetonitrile, or di*iso*propyl ether, different molecular complexities were found [2] but the value in each solvent was practically constant for the series of alkoxides. Thus it appeared that the chain length of the normal alkyl group had a negligible effect on the molecular complexity of the alkoxide. As a consequence of our theory [3] developed to explain the properties of the tetra-alkoxides of Group IVA metals, it was believed that the molecular complexity and volatility of tantalum penta-alkoxides would be strongly dependent on the degree of branching of the alkyl group. To test this and to extend our knowledge of tantalum alkoxides the new isomeric butoxides and isomeric pentyloxides were prepared and their molecular weights and volatilities determined. The phenomenon of alcohol interchange involving tantalum alkoxides was demonstrated by the preparation of the alkoxides of *n*- and *iso*-pentyl alcohol by the following reactions :

$$Ta(O{\cdot}CH_2{\cdot}CH{\cdot}MeEt)_5 + 5CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH \longrightarrow Ta(O{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2)_5 + 5CHMeEt{\cdot}CH_2{\cdot}OH$$

$$Ta(O{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe_2)_5 + 5n\text{-}C_5H_{11}{\cdot}OH \longrightarrow Ta(O{\cdot}C_5H_{11}\text{-}n)_5 + 5CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$$

The other tantalum alkoxides were obtained by reactions involving tantalum pentachloride and the appropriate alcohol in the presence of excess of ammonia :

$$TaCl_5 + 5ROH + 5NH_3 \longrightarrow Ta(OR)_5 + 5NH_4Cl$$

When secondary or tertiary alcohols were used an excess of pyridine was added to the pentachloride before the addition of the alcohol. This procedure obviated side reactions which occurred in the absence of pyridine.

Isomeric Pentabutoxides of Tantalum.—The normal physical appearance of the butoxides did not change regularly with the extent of chain branching of the butyl group. Thus the normal and secondary butoxides were pale yellow mobile liquids at room temperature but the *iso*butoxide (m. p. *ca.* 157°) and the tertiary butoxide (m. p. 110°) were solid. The high melting point of the *iso*butoxide made it necessary to determine boiling points of the butoxides under 5·5 mm. pressure for comparative purposes. These data and the molecular weights in benzene are shown in Table 1. They confirm the expected increase in volatility with increased branching of the butyl group. However, the increment in boiling point (ΔT_B) from one isomer to the next shows an abrupt change when passing from the *iso*butoxide to the *sec.*-butoxide. Further, this effect is clearly reflected, at the same point, in the molecular complexities. Hence it appears that polymerisation, a consistent feature

TABLE 1.

R in $Ta(OR)_5$	B. p./5·5 mm.	ΔT_B	*M*	Mol. complexity
$Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}$	242°	—	1102 [a]	2·02
$Me_2CH{\cdot}CH_2{\cdot}$	210	32°	1094 [a]	2·00
$Me{\cdot}CH_2{\cdot}CHMe{\cdot}$	156	54	593 [a]	1·06
$Me_3C{\cdot}$	149·5	6	554 [b]	1·01

[a] Ebullioscopic method. [b] Cryoscopic method.

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* Part IV, *J.*, 1953, 2025.

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

[2] *Idem*, *J.*, 1956, 5.

[3] Bradley, Mehrotra, and Wardlaw, *J.*, 1952, 2027, 4204, 5020; Bradley, Mehrotra, Swanwick, and Wardlaw, *J*, 1953, 2025; Bradley, Saad, and Wardlaw, *J.*, 1954, 3488.

of tantalum *n*-alkoxides, is prevented in the secondary and tertiary butoxides by the steric effect of branched butyl groups. The small difference in the boiling points (ΔT_B 6°) of the *sec.*- and *tert.*-butoxides is clearly a consequence of their monomeric nature which would cause a similarity in intermolecular forces. The higher melting point of the *tert.*-butoxide is especially interesting and suggests that this compound, by virtue of its more compact and nearly spherical molecules, possesses greater rotational freedom than the *sec.*-butoxide in the solid state. Earlier work on the Group IVA alkoxides established[3] that the two main factors which determined the volatility and molecular complexity of metal alkoxides were (i) the degree of branching and size of alkyl group and (ii) the atomic radius of the central atom. According to Sidgwick,[4] the atomic radii of tantalum and titanium are 1·34 and 1·36 Å respectively and therefore a comparison of tantalum penta-alkoxides with the corresponding tetra-alkoxides of titanium should reveal the part played by a new factor, *i.e.*, the number of groups attached to the central atom. The boiling points of titanium isomeric butoxides under 0·1 mm. pressure are[3]: *n* 142°; *iso* 106°; *sec.* 81°; *tert.* 50°. In this series it is noteworthy that the volatility increases steadily with increased branching of the butyl group from normal to tertiary in contrast to the abrupt change from *iso*- to *sec.*-butoxide for the tantalum derivatives. This shows the greater screening effect of five alkoxide groups in the tantalum compounds compared with four of the same alkoxides in the titanium compounds. Comparing monomeric compounds, it is not surprising to find that titanium tetra-*tert.*-butoxide $TiO_4C_{16}H_{36}$ (b. p. 96°/5·7 mm.), which has 57 atoms per molecule, has a lower boiling point than tantalum penta-*tert.*-butoxide $TaO_5C_{20}H_{45}$ (b. p. 149·5°/5·5 mm.) which has 71 atoms per molecule. On the other hand titanium tetra-*tert.*-pentyloxide, which has 69 atoms per molecule, has a boiling point (143°/5·0 mm.) quite close to that of tantalum penta-*tert.*-butoxide and the small difference could easily be due to the additional oxygen and hydrogen atoms in the tantalum compound. Thus the following centrosymmetrical molecules give rise to liquids of similar volatility: $Ti(O{\cdot}CMe_2Et)_4$; $Zr(O{\cdot}CMe_2Et)_4$; $Hf(O{\cdot}CMe_2Et)_4$; $Ta(O{\cdot}CMe_3)_5$. This behaviour is in accord with our theory that in these molecules the central metal atom is so effectively screened by its organic envelope that it can make only a minor contribution to the energy of intermolecular attraction in the liquid state. The major contribution must arise from interactions involving the peripheral carbon and hydrogen atoms, whilst the atomic weight or valency of the metal atom is relatively unimportant.

In view of the interesting behaviour of tantalum normal alkoxides in their own alcohols[2] the molecular weight of the *iso*butoxide was determined in boiling *iso*butyl alcohol (b. p. 107°). The molecular complexity found (1·47) was significantly higher than that (1·40) of the *n*-butoxide in *n*-butanol (b. p. 117°). If it is assumed that the donor tendencies of these alcohols are very similar, it appears that the lower complexity of the *n*-butoxide is caused by the higher boiling point of *n*-butanol, because any stereochemical effect due to chain branching in the *iso*butoxide or *iso*butyl alcohol would tend to lower the complexity of the *iso*butoxide. This supports our previous conclusion[2] that the molecular complexity of an alkoxide in its own alcohol is mainly determined by the boiling point and donor power of the alcohol.

TABLE 2.

R in $Ta(OR)_5$	Appearance	B. p./0·1 mm.	ΔT_B	*M*	Mol. complexity
$Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}$	Liquid	233°	—	1239	2·01
$Me_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}$	,,	210	23°	1223	1·98
$MeEtCH{\cdot}CH_2{\cdot}$	Very viscous	204	6	1216	1·97
$Me_3C{\cdot}CH_2{\cdot}$	Solid (m. p. 90°)	130	74	831	1·35
$Et_2CH{\cdot}$	Very viscous	153	(—)23	626	1·02
$MePr^nCH{\cdot}$	Liquid	148	5	614	0·99
$MePr^iCH{\cdot}$	Viscous	137	11	625	1·02
$Me_2EtC{\cdot}$	,,	139	(—)2	619	1·00

Isomeric Pentapentyloxides of Tantalum.—The data on the pentyloxides are set out in Table 2. The molecular weights were determined ebullioscopically in benzene. Again

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[4] Sidgwick, "Chemical Elements and their Compounds," Clarendon Press, Oxford, 1950, Vol. I, p. xxix.

it is evident that increased branching of the alkyl groups causes a decrease in molecular complexity and an increase in volatility. Considering first the primary pentyloxides, the behaviour of the *neo*pentyloxide is outstanding since it is the only primary derivative exhibiting a molecular complexity appreciably less than two and it is strikingly more volatile than any of the others. In fact, the *neo*pentyloxide is even more volatile than the monomeric secondary or tertiary pentyloxides, and its molecular complexity of 1·35 in boiling benzene seemed anomalously high. However, repeated ebullioscopic determinations of the molecular weight gave the same result whilst cryoscopic measurements in benzene gave a value of 1·39 for the complexity. This anomalous polymerisation of the *neo*pentyloxide is not confined to the tantalum derivative because earlier work[3] on the Group IVA alkoxides showed a similar but less pronounced effect in the pentyloxides of titanium and zirconium. Thus titanium tetra*neo*pentyloxide (m. p. 64°), with a molecular complexity of 1·3 in boiling benzene, was more volatile than the liquid monomeric secondary pentyloxides. In the case of zirconium the *neo*pentyloxide (m. p. 150—160°) had a complexity of 2·4 although it was close in volatility to the dimeric secondary pentyloxides. It is significant that the *neo*pentyloxides of titanium, tantalum, and zirconium are crystalline, with relatively high melting points compared with the corresponding secondary pentyloxides. Hence the anomalous complexities of the *neo*pentyloxides may not be caused by intermolecular forces between metal and oxygen but instead may be due to the factors which produce the high melting points of these compounds. In particular we believe that the high melting points arise from the compactness and nearly spherical nature of alkoxides containing the *neo*pentyl group (cf. the behaviour of secondary and tertiary butoxides of tantalum). A comparison of the primary pentyloxides of tantalum (Table 2) with the isomeric butoxides (Table 1) reveals the greater screening achieved by branching at the carbinol-carbon compared with similar branching at the β-carbon of the alkoxide group. Thus, for the butoxides an abrupt change in volatility and molecular complexity occurs between the *iso*butoxide and *sec.*-butoxide while in the primary pentyloxides a similar change occurs between the derivatives of *iso*pentyl and *neo*pentyl alcohol.

It is not surprising to find that all the secondary pentyloxides of tantalum are monomeric and consequently close in volatility to the monomeric tertiary pentyloxide. In fact the order of volatilities of the monomeric pentyloxides is: $Me_2EtC \sim MePr^iCH > MePr^nCH > Et_2CH$. We have already suggested that the monomeric penta-*tert.*-butoxide of tantalum should have a similar boiling point to the monomeric tetra(tertiary pentyloxides) of titanium, zirconium, and hafnium. For the same reason we should expect the boiling point of the tertiary pentyloxide of tantalum to be near to the boiling points of the monomeric tetrahexyloxides of titanium and zirconium. From previous work[3] the following boiling points under 0·1 mm. pressure have been calculated: $Ti(O{\cdot}CMeEt_2)_4$ 128°; $Zr(O{\cdot}CMeEt_2)_4$ 130°; $Ti(O{\cdot}CHEtPr^n)_4$ 134°; $Ti(O{\cdot}CHMeBu^n)_4$ 126°; $Ti(O{\cdot}CHMeBu^t)_4$ 127°; $Zr(O{\cdot}CHMeBu^t)_4$ 128°. It appears that the boiling points for monomeric hexyloxides of titanium and zirconium are *ca.* 130°/0·1 mm. and compare well with $Ta(O{\cdot}CHMePr^i)_5$ 137°/0·1 mm. and $Ta(O{\cdot}CMe_2Et)_5$ 139°/0·1 mm.

EXPERIMENTAL

Details of the experimental technique and apparatus have already been described.[1,3] *tert.*-Butyl alcohol was dried by refluxing it over quick-lime, distilling, and refluxing the distillate over sodium. The other alcohols were fractionally distilled and the purest fractions were dried azeotropically with benzene. Pyridine ("AnalaR") was refluxed over potassium hydroxide (pellets), then distilled, and the distillate dried azeotropically with benzene.

*Tantalum Penta*iso*pentyloxide*.—Benzene (100 c.c.) and *iso*pentyl alcohol (30 c.c.) were added to tantalum penta-2-methylbutoxide (10 g.; preparation given below), and alcohol interchange was effected by fractional distillation. After evaporation of the residual solvent the new *alkoxide* was distilled (b. p. 210°/0·1 mm.) [Found: Ta, 29·3. $Ta(OC_5H_{11})_5$ requires Ta, 29·4%].

Tantalum Penta-n-*pentyloxide*.—Alcohol interchange was conducted on a mixture of tantalum penta*iso*pentyloxide (7 g.), benzene (100 c.c.), and *n*-pentyl alcohol (20 c.c.) in the foregoing manner. The new *alkoxide* distilled at 239°/0·2 mm. (Found: Ta, 29·3%).

Preparation of Tantalum Alkoxides from the Pentachloride.—Details of the preparation by the ammonia method in the absence of pyridine have been reported.[1] When pyridine was used the procedure was modified in order to complete the removal of chloride. The following preparation of tantalum penta-*tert.*-butoxide is typical: Pyridine (200 c.c.) and *tert.*-butyl alcohol (20 c.c.) were allowed to react with tantalum pentachloride (10 g.), and the solution was treated with ammonia in excess. After filtration and evaporation of solvent a white solid (Found: Cl, 0·39%) remained. This was dissolved in *tert.*-butyl alcohol (20 c.c.) and benzene (100 c.c.) and treated with ammonia. Removal of the finely divided ammonium chloride was effected with the aid of "Hyflo-supercel" and a sintered glass filter (porosity no. 4). The filtrate was evaporated to dryness and gave a chloride-free wax (10 g.) [Found: Ta: 33·1; $Ta(OC_4H_9)_5$ requires Ta 33·1%]. A sample sublimed unchanged at 82°/0·05 mm. The remainder of the results are presented in Table 3.

TABLE 3.

R	ROH (c.c.)	$TaCl_5$ (c.c.)	C_5H_5N (c.c.)	C_6H_6 (c.c.)	$Ta(OR)_5$ Yield (g.)	B. p.°/mm.	Found: Ta (%)
$Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}$	20	10·0	—	200	14·0	217/0·15 242/5·5	33·16
$Me_2CH{\cdot}CH_2{\cdot}$	20	10·0	—	200	13·5	155/0·1 (subl.) 210/5·5	33·2
$MeEt{\cdot}CH{\cdot}$	40	10·0	100	150	10·0	123/0·02 156/5·5	33·0
$MeEtCH{\cdot}CH_2{\cdot}$	40	10·0	—	200	14·0	206/0·15	29·3
$Me_3C{\cdot}CH_2{\cdot}$	15	10·0	—	150	15·0	136/0·2	29·3
$Et_2CH{\cdot}$	10	5·0	150	—	5·0	168/0·6	29·3
$MePr^nCH{\cdot}$	10	5·0	100	—	6·0	148/0·1	29·4
$MePr^iCH{\cdot}$	10	5·0	100	—	4·0	137/0·1	29·3
$Me_2EtC{\cdot}$	60	10·0	200	100	14·5	145/0·2	29·4

Molecular Weights.—The ebulliometric method has already been described [1, 2] and the results are given in Table 4. They include an anomalously high value (1·46) for the complexity of tantalum tetra-*tert.*-butoxide, due to the appreciable volatility of this compound in boiling benzene as proved by the detection of tantalum in the distillate.

TABLE 4.

R in $Ta(OR)_5$	Range of m (g.)	Benzene (g.)	$\Delta T/m$	M Found	M Calc.
$Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}$	0·075—0·290	15·93	0·168°	1102	546
$Me_2CH{\cdot}CH_2{\cdot}$	0·047—0·298	15·50	0·174	1094	,,
$MeEtCH{\cdot}$	0·080—0·320	15·59	0·329	575	,,
$Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$	0·063—0·387	16·20	0·147	1239	616
$Me_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}$	0·057—0·244	15·77	0·153	1223	,,
$MeEtCH{\cdot}CH_2$	0·055—0·278	16·18	0·150	1216	,,
$Me_3C{\cdot}CH_2{\cdot}$	0·042—0·250	15·92	0·223	831	,,
$Et_2CH{\cdot}$	0·048—0·455	16·51	0·285	627	,,
$MePr^nCH{\cdot}$	0·059—0·326	15·31	0·314	614	,,
$MePr^iCH{\cdot}$	0·038—0·205	16·30	0·289	625	,,
$Me_2EtC{\cdot}$	0·045—0·390	14·70	0·324	619	,,

Cryoscopic Determinations.—Molecular weights of the *tert.*-butoxide and the *neo*pentyloxide were determined cryoscopically in benzene, in an apparatus designed to exclude moisture. The results are given in Table 5.

TABLE 5.

R in $Ta(OR)_5$	Benzene (g.)	Alkoxide: m (g.)	$\Delta T°$	M Found	R in $Ta(OR)_5$	Benzene (g.)	Alkoxide: m (g.)	$\Delta T°$	M Found
$Me_3C{\cdot}$	14·90	0·153	0·095	552	$Me_3C{\cdot}CH_2{\cdot}$	14·62	0·124	0·050	867
		0·340	0·210	556			0·340	0·140	851
		0·450	0·280	553			0·470	0·190	866
			Calc.:	546				Calc.:	616

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BIRKBECK COLLEGE, MALET STREET,
LONDON, W.C.1.

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