Normal Alkoxides of Quinquevalent Tantalum.

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Tantalum penta-alkoxides, $Ta(OR)_5$ where $R = Me$, Et, Pr^n, or Bu^n, have been prepared by the action of an alcohol and ammonia on tantalum pentachloride. Ebullioscopic measurements showed that the alkoxides were dimers in benzene, but in the parent alcohols the complexity depended on the alcohol. These data together with the boiling points under reduced pressure are discussed from the theoretical standpoint.

IN recent communications the results of a study of the tetra-alkoxides of group IVA elements have been recorded and the properties of these substances have been interpreted on a stereochemical basis. This involves the tendency of the central atom to increase its covalency by intermolecular bonding, which is opposed by the rotation of the alkoxide groups screening the central atom. To ascertain how widely this theory can be applied we have now studied the alkoxides of group V elements. We have confirmed that the reaction between tantalum pentachloride and alcohol yields hydrogen chloride and tantalum dichloride triethoxide $TaCl_2(OEt)_3$. The greater reactivity of tantalum pentachloride than of zirconium or hafnium tetrachloride is expected from the reactivity theory proposed by Bradley, Halim, and Wardlaw (*J.*, 1950, 3450). Thus the greater inductive effect of five than of four chlorine atoms attached to a central atom should cause an enhanced fractional positive charge on tantalum compared with zirconium and hafnium.

The literature contains no mention of the preparation and properties of tantalum penta-alkoxides. A range of normal penta-alkoxides of tantalum has now been prepared and examined. The following quantitative reactions take place:

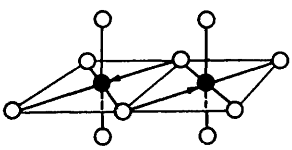
$$TaCl_5 + 5NH_3 + 5ROH \longrightarrow Ta(OR)_5 + 5NH_4Cl \quad (R = Me, Et, Pr^n, \text{ or } Bu^n)$$

These alkoxides are colourless mobile liquids at room temperature [except $Ta(OMe)_5$, m. p. 50°]. They are extremely readily hydrolysed to tantalum pentoxide but can be distilled under reduced pressure without decomposition. Their molecular weights have been determined ebullioscopically in benzene and in their parent alcohols (see Table 1).

TABLE 1.

R in Ta(OR)$_5$	B. p./10 mm.	*M*, in C_6H_6	*M*, in ROH	Mol. complexity in C_6H_6	Mol. complexity in ROH
CH_3	189°	664	404	1·98	1·20
C_2H_5	202	805	725	1·98	1·78
n-C_3H_7	232	927	809	1·95	1·70
n-C_4H_9	256	1102	763	2·02	1·40

Discussion.—The normal alkoxides of tantalum are dimeric in boiling benzene and show no change of complexity with concentration. This behaviour is readily explained on the assumption that tantalum attains a six-fold co-ordination with oxygen as shown inset. Moreover, it emphasises the contrast between quadrivalent and quinquevalent alkoxides in stereochemical requirements. For instance, in the case of zirconium alkoxides the lowest polymeric unit consistent with 6-co-ordinated zirconium is the trimer, higher polymers being possible, and experiments showed that the complexities of normal alkoxides of zirconium were between 3 and 4 (Bradley, Mehrotra, Swanwick, and Wardlaw, *J.*, 1953, 2025). The fifth alkoxide group present in tantalum alkoxides enables tantalum to realise the 6-co-ordinated state in the dimeric structure, which is the lowest possible polymer satisfying the stereochemical requirements. Further, the knowledge that tantalum normal alkoxides are dimeric in benzene solution enables us to rule out the possibility of tantalum's exhibiting a co-ordination number of 7 with oxygen in these compounds.



With regard to the molecular complexities of the alkoxides in their parent alcohols, two interesting points emerge. First, each alkoxide has a lower complexity in the alcohol than in benzene: this would be expected because the "donor" nature of the alcohols should favour monomeric alcoholates such as Ta(OR)$_5$,ROH in solution; however, it is noteworthy that no alcoholates were isolated under our experimental conditions. Secondly, the variation of molecular complexity with the alcohol is suprising. Thus the order of molecular complexities is $Ta(OMe)_5 < Ta(OEt)_5 > Ta(OPr^n)_5 > Ta(OBu^n)_5$. The chief factors determining this behaviour are probably boiling point, dielectric constant of the alcohol, and electron-donating tendency of the alcoholic oxygen. It seems improbable that stereochemical factors are important because these alkoxides are all dimeric in benzene. The effect of boiling point on molecular complexity should be in the sense that raising the boiling point will lower the complexity owing to thermal dissociation of the dimeric molecules. On this basis alone, the molecular complexity should steadily diminish from methyl alcohol to *n*-butyl alcohol but this is not the case and it suggests that last two factors are also important. It is hoped that studies now in progress of the effects of temperature, dielectric constant, and donor power of the solvent on the molecular complexity of the alkoxide will throw further light on this interesting problem.

With regard to the boiling points of the tantalum penta-alkoxides it is noteworthy that the increment (13°) between the methoxide and the ethoxide is much less than the increments (30°, 24°) between the other alkoxides in ascending order of molecular weights. Thus it appears that the methoxide has an anomalously high boiling point, probably owing to greater intermolecular forces. More information on this point should be provided by forthcoming vapour-pressure measurements.

EXPERIMENTAL

The apparatus and experimental technique used were essentially similar to those previously described in our work on the group IVA alkoxides (*loc. cit.*). Owing to the ease with which tantalum alkoxides are hydrolysed, special precautions (*J.*, 1954, 1091) were taken to avoid hydrolysis.

The tantalum pentachloride was commercially available, niobium-free material and was used without further purification.

Determinations of tantalum were effected by precipitating hydrated tantalum pentoxide which was collected on a Whatman filter paper (No. 41) and ignited and weighed as Ta_2O_5. The determinations of methoxide and ethoxide were carried out by methods previously described (*loc. cit.*).

Reaction between Tantalum Pentachloride and Ethyl Alcohol.—Addition of ethyl alcohol (50 c.c.) to tantalum pentachloride (5 g.) caused a vigorous reaction with evolution of hydrogen chloride. The solution was evaporated to dryness under reduced pressure with final drying at 90°/0·5 mm. The finely crystalline solid (5·5 g.) [Found: Ta, 48·0; Cl, 18·0. Calc. for $TaCl_2(OEt)_3$: Ta, 46·8; Cl, 18·3%] gave a clear solution in water.

Preparation of Tantalum Alkoxides.—The method involved the addition of the appropriate alcohol to a suspension of the pentachloride in benzene, followed by treatment with excess of ammonia. The ammonium chloride was filtered off, and the filtrate evaporated under reduced pressure. In all cases the chloride-free tantalum alkoxide produced was distilled under reduced pressure, and the distillate was analysed. The details of these experiments are given in Table 2. The b. p.s were determined under a pressure of 10 mm. in an all-glass hypsometer, and the data are reported in Table 1.

TABLE 2.

R	ROH taken (c.c.)	$TaCl_5$ taken (g.)	C_6H_6 (c.c.)	$Ta(OR)_5$ Yield (g.)	$Ta(OR)_5$ B. p./0·2 mm.	Found (%) Ta	Found (%) OR	Reqd. (%) Ta	Reqd. (%) OR
Me	45·0	17·0	250	13·9 *	130°	53·8	46·2	53·8	46·1
Et	25·0	10·0	200	11·0	147	44·2	55·2	44·6	55·4
Pr^n	30·0	10·0	200	10·5	184	38·0	62·0	38·0	62·0
Bu^n	35·0	10·0	200	13·0	217	33·2	—	33·1	—

* M. p. 50° C.

TABLE 3.

Alkoxide	Range of m (g.)	Solvent (g.)	$\Delta T/m$	M Found	M Calc.
$Ta(OMe)_5$	0·052—0·813	15·59 ^{a}	0·285°	664	336
,, ...	0·069—0·365	16·35 ^{b}	0·236	404	,,
$Ta(OEt)_5$	0·182—0·432	14·65 ^{a}	0·250	805	406
,, ...	0·042—0·542	14·25 ^{c}	0·106	725	,,
$Ta(OPr^n)_5$	0·060—0·328	16·07 ^{a}	0·198	927	476
,, ...	0·055—0·415	15·74 ^{d}	0·126	809	,,
$Ta(OBu^n)_5$	0·075—0·290	15·93 ^{a}	0·168	1102	546
,, ...	0·033—0·128	16·93 ^{e}	(95·0 mm. *)	763	',

^{a} Benzene; ^{b} methyl alcohol; ^{c} ethyl alcohol; ^{d} n-propyl alcohol; ^{e} n-butyl alcohol. * This boiling point elevation is in terms of mm. of water pressure difference in the water thermometer since no conversion tables are available for this temperature region.

Molecular Weights.—Molecular weights were determined in an all-glass ebulliometer incorporating a differential water-thermometer. The plot of $\Delta T°$ against weight of solute (m) was linear over the concentration range studied; the details are recorded in Table 3. An improved technique was devised to limit the error to ±0·5% and this will be described later.

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