19. *Niobium and Tantalum Mixed Alkoxides.*

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A number of volatile mixed alkoxides of tantalum of the type $Ta(OR)(OR')_4$, where R is a primary, secondary, or tertiary alkyl group and R′ is secondary or tertiary, have been prepared by alcohol interchange in the presence of excess of R′OH. The corresponding type of compound, with R′ = *tert.*-butyl, for niobium was unstable, giving rise to $Nb_2O(OBu^t)_8$ and $NbO(OBu^t)_3$. The penta*iso*propoxides of niobium and tantalum were also prepared.

In attempting to prepare tantalum penta*iso*propoxide by alcohol interchange of tantalum pentaethoxide with *iso*propyl alcohol we obtained a crystalline mixed alkoxide $Ta(OEt)(OPr^i)_4$ which sublimed unchanged under reduced pressure. The mixed alkoxide still remained despite prolonged treatment with excess of *iso*propyl alcohol. However, tantalum penta*iso*propoxide was obtained directly by the reaction of tantalum pentachloride, *iso*propyl alcohol, and ammonia. Similarly, tantalum penta-*tert.*-butoxide had been obtained[1] from the pentachloride by the ammonia method, yet the action of excess of *tert.*-butyl alcohol on tantalum pentaethoxide gave the volatile crystalline $Ta(OEt)(OBu^t)_4$. Further work revealed that the formation of tantalum mixed alkoxides is a general feature of alcohol interchange when the alcohol in excess is a secondary or tertiary alcohol, *viz.*,

$$Ta(OR)_5 + 4R'OH \longrightarrow Ta(OR)(OR')_4 + 4ROH$$

Some data on these compounds and the penta*iso*propoxide, penta-*tert.*-butoxide and penta-*tert.*-amyloxide are given in Table 1. The molecular complexities shown in parentheses are assumed values. For example, both $Ta(OEt)(OBu^t)_4$ and $Ta(OBu^t)_5$ were found to be monomeric, so $Ta(OPr^i)(OBu^t)_4$ must also be monomeric.

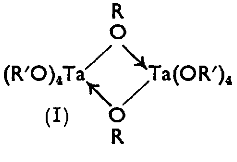
Table 1.

Compound	M. p.	Volatility *	Mol. complexity
$Ta(OMe)(OPr^i)_4$	70°	81°/0·07 mm.†	1·84
$Ta(OEt)(OPr^i)_4$	—	130/0·1 †	1·16
$Ta(OPr^i)_5$	84	122/0·1	0·99
$Ta(OMe)(OBu^t)_4$	110	96/0·05 †	1·00
$Ta(OEt)(OBu^t)_4$	96	84/0·05,† 128/5·5	0·99
$Ta(OPr^i)(OBu^t)_4$	94	86°/0·02 mm.	(1·0)
$Ta(OBu^t)_5$	110	82/0·02,† 149·5/5·5	1·01
$Ta(OEt)(OCMe_2Et)_4$	158	170/0·1	(1·0)
$Ta(OPr^i)(OCMe_2Et)_4$	90	139/0·1	(1·0)
$Ta(OCMe_2Et)_5$	—	142/0·1	1·01

* *I.e.*, boiling point or sublimation point (marked †).

The molecular weights were determined cryoscopically in benzene for all compounds except the penta-*tert.*-amyloxide which was determined ebullioscopically. Ebullioscopy gave anomalously high values for the other compounds owing to their appreciable volatility in boiling benzene.

The series $Ta(OR)(OPr^i)_4$, where R = Me, Et, or Pr^i, is of special interest because only one alkoxide group varies and it is the particular group involved in polymerisation by bridging, *i.e.*, inset (I). The results clearly show that the degree of dimerisation decreases with increase in size of the group OR in the order MeO > EtO > Pr^iO, expected on stereochemical grounds. The remaining compounds in Table 1 are monomeric and it is not surprising that they are relatively volatile. The high melting points suggest that these molecules rotate considerably in the crystalline state.



(I)

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[1] Bradley, Wardlaw, and Whitley, *J.*, 1956, 1139.

It is tempting to suggest that the formation of these mixed alkoxides is caused by steric effects because they are only formed where R′ is a branched alkyl group. The failure to replace the OR group in $Ta(OR)(OR')_4$ would then be due to repulsion of the incoming R′OH molecule by the other branched groups attached to the tantalum. This implies that alcohol interchange involves a bimolecular mechanism in which the incoming alcohol molecule becomes co-ordinated to the tantalum in the transition state. However, this simple explanation is inadequate, because, for example, the molecular weight shows that $Ta(OMe)(OPr^i)_4$ is predominantly dimeric. Now the steric hindrance to forming the dimer $Ta_2(OMe)_2(OPr^i)_8$ (assumed to be a binuclear octahedral complex) is very similar to that involved in the activated complex $Pr^iOH \rightarrow Ta(OMe)(OPr^i)_4$ and hence this transition state should be readily attained and interchange ought then to occur. More remarkable is the fact that interchange occurred between tantalum penta-*tert.*-butoxide and *tert.*-amyl alcohol with the formation of the mixed tertiary alkoxide $Ta(OBu^t)_2(OCMe_2Et)_3$. This being the case it seems probable that the treatment of, say, $Ta(OMe)(OPr^i)_4$ with excess of *iso*propyl alcohol leaves the methoxide group attached to tantalum because the *iso*propoxide groups are preferentially replaced. Amongst more work required to solve this problem is a knowledge of the structure of the monomeric tantalum penta-alkoxides.

Niobium resembled tantalum in behaviour in some of these reactions but differed in others. For example, niobium pentaethoxide with excess of *iso*propyl alcohol gave a niobium ethoxide *iso*propoxide. Also, niobium penta*iso*propoxide was readily prepared from the pentachloride, *iso*propyl alcohol, and ammonia. The penta*iso*propoxide (sublimes at 60—70°/0·1 mm.) is monomeric and apears to be more volatile than the corresponding tantalum compound. However, when niobium pentaethoxide was treated with *tert.*-butyl alcohol the ethoxide was all replaced but the product was an oxide *tert.*-butoxide near $Nb_2O(OBu^t)_8$ which, at 110—130°/0·01 mm., gave a sublimate of mainly $NbO(OBu^t)_3$. In a reaction of niobium *iso*propoxide with *tert.*-butyl alcohol in which the temperature did not exceed 40° the product, a mixture of $Nb(OPr^i)(OBu^t)_4$ and $Nb_2O(OBu^t)_8$, showed that decomposition had occurred. This behaviour of niobium alkoxides with *tert.*-butyl alcohol is similar to that of niobium pentachloride with *tert.*-butyl alcohol in the presence of pyridine and ammonia.[2] No penta-*tert.*-butoxide was isolated, but a niobium oxide *tert.*-butoxide was obtained. The present results show that niobium *tert.*-butoxides are unstable irrespective of whether they are prepared from the pentachloride or by alcohol interchange on a penta-alkoxide.

EXPERIMENTAL

Preparation of Mixed Alkoxides of Tantalum.—Tantalum penta-methoxide, -ethoxide, -*tert.*-butoxide, and -*tert.*-amyloxide were prepared as already described.[1,3] The mixed alkoxides were then obtained by alcohol interchange in benzene with removal of the liberated alcohol by azeotropic fractional distillation. The solution was evaporated to dryness under reduced pressure and the solid product sublimed in a molecular still. Details are given in Table 2.

TABLE 2.

	$Ta(OR)_5$		R′OH	C_6H_6	$Ta(OR)(OR')_4$	OR (%)		Ta (%)	
R	(g.)	R′	(g.)	(c.c.)	(g.)	Found	Calc.	Found	Calc.
Me	3·5	Pr^i	35·0	150	4·5	—	—	40·4	40·4
Et	4·0	Pr^i	37·8	150	4·5	—	—	39·2	39·1
Me	3·5	Bu^t	150 *	—	5·0	6·0	6·1	35·7	35·9
Et	3·7	Bu^t	150 *	—	5·1	8·7	8·7	35·0	34·9
Pr^i	3·0	Bu^t	180 *	—	3·4	11·7	11·1	33·8	34·0
Et	3·0	CMe_2Et	53·6	100	4·0	7·9	7·8	31·4	31·5
Pr^i	4·0	CMe_2Et	10·5	50	4·5	9·8	10·0	30·7	30·7

* Benzene–*tert.*-butyl alcohol azeotrope.

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

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

*Preparation of Tantalum Penta*iso*propoxide.*—Tantalum pentachloride (5·0 g.) was added to *iso*propyl alcohol (15 c.c.) and benzene (100 c.c.) and the solution was treated with excess of ammonia. After filtering off the ammonium chloride and evaporating the filtrate to dryness under reduced pressure we obtained white crystals (5·2 g.) of the *penta*iso*propoxide*, m. p. 84°; it was distilled at 122°/0·1 mm. [Found: Ta, 37·8; Pr^iO, 61·8. $Ta(OPr^i)_5$ requires Ta, 38·0; Pr^iO, 62·0%].

Reaction of Tantalum tert.*-Butoxide with* tert.*-Amyl Alcohol.*—To the solution of tantalum *tert.*-butoxide (3 g.) in benzene (50 c.c.) was added *tert.*-amyl alcohol (5·0 c.c.) and the mixture was fractionally distilled. The appearance of the benzene–*tert.*-butyl alcohol azeotrope indicated a replacement. When no more azeotrope was produced the solution was evaporated under reduced pressure to give *tantalum tri-*tert.*-amyloxide di-*tert.*-butoxide* as a viscous liquid (3·2 g.) [Found: Ta, 30·7. $Ta(OBu^t)_2(OCMe_2Et)_3$ requires Ta, 30·8%].

*Preparation of Niobium Penta*iso*propoxide.*—Niobium pentachloride (28·7 g.) was added to *iso*propyl alcohol (100 c.c.) and benzene (250 c.c.) and the solution was treated with excess of ammonia. After the removal of ammonium chloride and solvent in the usual manner a grey-blue solid (30·6 g.) remained. This was washed four times with cold *iso*propyl alcohol (25 c.c.) to remove the colour and the residue was sublimed at 60—80°/0·1 mm. The white sublimate of *niobium penta*iso*propoxide* recrystallised from boiling *iso*propyl alcohol [Found: Nb, 24·1; Pr^iO, 75·0. $Nb(OPr^i)_5$ requires Nb, 24·0; Pr^iO, 76·0%].

Reaction of Niobium Ethoxide with tert.*-Butyl Alcohol.*—Niobium pentaethoxide [4] (3·9 g.) in benzene (150 c.c.) was treated with *tert.*-butyl alcohol until no more benzene–ethyl alcohol azeotrope could be separated by fractional distillation. Removal of excess of *tert.*-butyl alcohol and solvent under reduced pressure left crystals of the *oxide* tert.*-butoxide* (3·8 g.) [Found: Nb, 24·1; EtO, 0. $Nb_2O(OBu^t)_8$ requires Nb, 23·6%]. This product was sublimed at 110 130°/0·01 mm. in a molecular still to yield another *oxide* tert.*-butoxide* [Found: Nb, 27·8. $NbO(OBu^t)_3$ requires Nb, 28·3%]. A small amount of non-volatile residue with a high niobium content (39·7%) remained.

Reaction of Niobium iso*Propoxide with* tert.*-Butyl Alcohol.*—Niobium penta*iso*propoxide (2·5 g.) was dissolved in benzene–*tert.*-butyl alcohol azeotrope (100 c.c.) at room temperature and the solvent and mixture of alcohols were then evaporated under reduced pressure below 45°. White crystals of the *oxide* tert.*-butoxide* iso*propoxide* (3·3 g.) remained [Found: Nb, 21·3; Pr^iO, 4·8. $Nb_3O(OPr^i)(OBu^t)_{12}$ requires Nb, 22·6; Pr^iO, 4·8%].

Molecular Weight.—An all-glass freezing-point apparatus incorporating a Beckmann thermometer was used with benzene as solvent. Results are given in Table 3.

TABLE 3.

Compound	Wt. of cpd. (g.)	Wt. of C_6H_6 (g.)	F. p. depression	*M*	
				Found	Calc.
$Ta(OMe)(OPr^i)_4$	0·5654	39·12	0·089°	829·5	448·3
	0·8082	,,	0·129	818·0	,,
$Ta(OEt)(OPr^i)_4$	0·3874	45·63	0·081	536·0	462·3
	0·7991	,,	0·166	539·0	,,
$Ta(OPr^i)_5$	0·250	12·35	0·220	472	476
	0·426	,,	0·370	472	,,
	0·622	,,	0·540	473	,,
$Ta(OMe)(OBu^t)_4$	1·007	43·87	0·239	492·0	504·4
	1·878	,,	0·440	498·0	,,
$Ta(OEt)(OBu^t)_4$	0·4255	57·33	0·075	507·0	518·4
	0·9628	,,	0·165	521·0	,,
$Nb(OPr^i)_5$	0·9349	40·60	0·305	386·5	388·4
	1·8236	,,	0·584	393·8	,,

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