ORGANIC COMPOUNDS OF NIOBIUM AND TANTALUM

ALCOHOLYSIS REACTIONS OF NIOBIUM AND TANTALUM PENTA-ALKOXIDES

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SUMMARY

Reactions of niobium and tantalum penta-ethoxides with *n*- and isopropanols, *n*-, *sec.*- and *tert.*-butanols and *tert.*-pentanol have been studied. In order to make a comparative study of the reactivities of primary, *sec.*- and *tert.*-alcohols, the reactions of niobium and tantalum penta-alkoxides (methoxides, ethoxides and isopropoxides) with *tert.*-butanol, and niobium and tantalum penta-*tert.*-butoxides with alcohols (methanol, ethanol and isopropanol) have been studied and products of the type $M(OBut)(OR)_4$ (where M is niobium or tantalum) obtained. However, the reactions of penta-methoxides with *tert.*-butanol yield finally $M(OBut)_{1.5}(OMe)_{3.5}$. The identity of these mixed alkoxides has been established by distilling or subliming them under reduced pressure. Molecular weights of these mixed alkoxides were determined ebullioscopically in benzene.

INTRODUCTION

BRADLEY and co-workers¹ synthesised a number of niobium penta-alkoxides (*n*-butoxide, *n*-pentyloxide and neopentyloxide) from niobium penta-ethoxide by an alcohol interchange technique. In an attempt to prepare niobium and tantalum penta-isopropoxides by alcohol interchange of penta-ethoxides with isopropanol, BRADLEY and co-workers² obtained mixed alkoxides of the type $M(OEt)(OPr^i)_4$. A similar mixed derivative was obtained in the reaction of tantalum penta-ethoxide with *tert*.-butanol². The non-formation of the penta-alkoxide derivatives with isopropanol and *tert*.-butanol would thus appear to be caused by steric factors. However, the preparation of penta-sec.-butoxides from niobium and tantalum pentamethoxides by BRADLEY AND HOLLOWAY³ has led BRADLEY⁴ himself to doubt the validity of their earlier observations.

The reaction of niobium penta-ethoxide with *tert*.-butanol as well as that of pentachloride with *tert*.-butanol in the presence of pyridine and ammonia by BRAD-LEY and co-workers^{1,2} was found to be rather complicated and final end products were

reported to be oxide *tert.*-butoxide. However, THOMAS⁵ has been successful in the synthesis of niobium penta-*tert.*-butoxide by the reaction of niobium tetra-dialkylamide with *tert.*-butanol. We have also prepared the niobium penta-*tert.*-butoxide by a transesterification technique⁶. The penta-*tert.*-butoxide could be sublimed unchanged at about 90°C under 0.1 mm pressure.

In view of the above results, it was considered of interest to re-investigate the alcoholysis reactions of niobium and tantalum penta-ethoxides. During the course of the present study, reactions of niobium and tantalum penta-ethoxides with *n*- and isopropanols, *n*-, *sec.*- and *tert.*-butanols and *tert.*-pentanol have been studied. It has been found that reactions of *n*- and *sec.*-alcohols with niobium penta-ethoxide are straightforward, yielding the corresponding penta-alkoxides. However, with tantalum, the products corresponded in all cases to the mixed alkoxides $Ta(OEt)(OR)_4$ with the exception of *sec.*-butanol where the penta-*sec.*-butoxide was obtained. The reactions with *tert.*-alcohols (butanol and pentanol) were found to be slow towards the end and the final products in both cases were the mixed alkoxides of the type $M(OEt)(OAm^t)_4$ with *tert.*-pentanol. However, in the case of *tert.*-butanol the reactions could be carried to completion and almost pure penta-*tert.*-butoxides (mixed with a small amount of $M(OEt)(OBu^t)_4$) could be obtained for both the elements.

TABLE 1

MOLECULAR COMPLEXITIES OF MIXED ALKOXIDES OF NIOBIUM AND TANTALUM

Product	Molecular weight		Molecular	
	Found	Calc.	complexity	
Nb(OEt)(OAm ^t) ₄	577	486	1.18	
$Ta(OEt)(OPr^n)_4$	951	462	2.05	
$Ta(OEt)(OPr^i)_4$	895	462	1.93	
$Ta(OEt)(OBu^n)_4$	1020	518	1.96	
$Ta(OEt)(OAm^{t})_{4}$	666	574	1.15	
Nb(OBu ^t)(OMe) ₄	596	290	2.05	
Nb(OBu ^t)(OEt) ₄	699	346	2.02	
Nb(OBu ^t)(OPr ⁱ) ₄	466	402	1.15	
Ta(OBu ¹)(OMe) ₄	781	378	2.07	
Ta(OBu ^t)(OEt) ₄	882	434	2.03	
Ta(OBu ^t)(OPr ⁱ) ₄	594	490	1.21	

Molecular weights of the mixed alkoxides obtained in the alcohol interchange reactions were determined ebullioscopically in benzene and were found to be dimeric except in the cases of $M(OEt)(OAm^t)_4$ (where M is niobium or tantalum) which were found to be essentially monomeric (Table I). BRADLEY and co-workers^{1,2,7} have reported that all the normal alkoxides of niobium and tantalum are dimeric, whereas *sec.*- and *tert.*-alkoxides are monomeric in benzene. The powerful shielding of the central metal atom by branched alkoxide groups prevents strong intermolecular bonding in the *sec.*- and *tert.*-alkoxides. Molecular weight determinations of Ta(OEt)-(OBu^s)₄ and Ta(OEt)(OBu^t)₄ showed them to have average molecular complexities of 1.4 and 1.2 respectively⁸.

It appears that in the case of tantalum, the tantalum atoms are so well shielded in the dimeric structure :



(where R is Pr^n , Pr^i or Bu^n) of the mixed alkoxides, that further coordination with reacting alcohol molecules becomes sterically hindered. However, greater hindrance would be expected in the reactions of tantalum penta-ethoxide with *sec.-* and *tert.*butanols. Although the reactions become markedly slow towards the end, they can be carried to completion with the formation of penta-*sec.-* and *tert.-*butoxides. However, increased steric hindrance of the bulkier *tert.-*pentyl groups appears to preclude the initial coordination to such a degree that further interchange of *tert.-*pentanol with $M(OEt)(OAm^t)_4$ could not be effected at all. Similar observations have already been made by MEHROTRA in the case of aluminium⁹ and zirconium¹⁰ alkoxides. In addition to steric factors, the energitics of the reactions also appears to play an important role.

The observed molecular complexities of $Ta(OEt)(OBu^s)_4$, $Ta(OEt)(OBu^t)_4$ and $Ta(OEt)(OAm^t)_4$ show that increased hindrance to the intermolecular polymerisation in these cases does not allow the dimerisation equilibrium to proceed almost to the side of the dimeric units as is found in the cases of $Ta(OEt)(OPr^n)_4$, $Ta(OEt)(OPr^i)_4$ and $Ta(OEt)(OBu^n)_4$. The extent of dimerisation equilibrium (1.4, 1.2 and 1.15 in the cases of $Ta(OEt)(OBu^s)_4$, $Ta(OEt)(OBu^s)_4$, $Ta(OEt)(OBu^t)_4$ and $Ta(OEt)(OAm^t)_4$ respectively) reflects the increasing effectiveness of the shielding of the central tantalum atom in the monomeric species. The increasing extent of this shielding also reduces the respective rates of their reactivities with the alcohol concerned, *i.e.*, Bu^sOH, Bu^tOH and Am^tOH. Under the experimental conditions employed, the reaction could be carried to completion in the two former cases.

A similar observation has already been made in the reactions of niobium and tantalum penta-ethoxides with organic esters^{6,8}. In view of the closely agreeing values (1.34 Å) reported¹¹ for the atomic radii of niobium and tantalum, this difference in the behaviour of their penta-ethoxides towards alcoholysis reactions of normal alcohols appears to be due to electronic factors.

MEHROTRA AND VARMA¹² have attempted to make a systematic study of the comparative reactivities of primary, secondary and tertiary alcohols with titanium alkoxides which follow the order MeOH > EtOH > Pr⁴OH > Bu⁴OH. Similar observations have already been made in the cases of zirconium¹³ and tin¹⁴ alkoxides. In view of the above, it was considered of interest to extend similar studies to niobium and tantalum. Mixed alkoxides of niobium and tantalum with the formula $M(OBu^t)(OR)_4$ can be conveniently synthesised by treating the pent-methoxides, ethoxides and isopropoxides with *tert*.-butanol, and *tert*.-butoxides with alcohols (methanol, ethanol and isopropanol) in molar ratio of 1:5 in benzene at room temperature. The reactions of penta-methoxides and *tert*.-butanol appeared to be slightly different, having the composition $M(OBu^t)_{1.5}(OMe)_{8.5}$. The identity of these mixed alkoxides has been established by distilling or subliming them unchanged and their molecular weights have been determined in boiling benzene.

The reactions of niobium and tantalum penta-tert.-butoxides with methanol and ethanol were found to be exothermic.

REACTIONS OF	NIOBIUM PENTA-ETHOXII	DE WITH ALCOHOLS IN BENZENE				
Nb(OEt)5 (g)	Alcohol	Product, yield and state	b.p. (°C(mm)	Yield of distilled	Analysis Nb	versenter a subman a resonance
				(0) annort	Found (%)	Calc. (%)
2.18	n-propanol (6.8 g)	$Nb(OPt^n)_{\delta}$ (2.66 g); orange-yellow liquid.	171/0.4	84	24.6	23.9
2.65	isopropanol (7.6 g)	Nb(OPr ⁽) ₅ (3.23 g); white, crystalline solid.	90100/0.5	64	24.6 isopropoxy = 76.2	23.9 isopropoxy = 76.1
2.24	<i>n</i> -butanol (6.1 g)	Nb(OBu ⁿ) ₅ (3.32 g); yellow, viscous liquid.	198/0.3	73	20.7	20.3
2.72	secbutanol (5.9 g)	Nb(OBu*)5 (3.92 g); yellow liquid.	114/0.2	86	20.3	20.3
2.31	<i>tert.</i> -butanol (8.9 g)	Nb(UBut)s* (3.32 g) white, crystalline solid.	110-120/0.7	50	21.0	20.3
3.25	<i>tert</i> pentanol (10.38 g)	Nb(OEt)(OAm ^t) ₄ (5.18 g) colourless, pasty liquid.	148/0.4	81	19.5 ethoxy = 8.6	19.1 ethoxy = 9.3
* Contains 2.4	% ethoxy in sublimed p	oduct.				and the second

TABLE II

ALCOHOLYSIS REACTIONS OF NIOBIUM AND TANTALUM PENTA-ALKOXIDES

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$M(OBu^t)_5 + 5ROH \rightarrow M(OBu^t)(OR)_4 + ROH + 4Bu^tOH$

(M is either niobium or tantalum)

Evidently the above reactions occur in two stages; firstly the *tert*.-butoxide group is replaced by primary alkoxide group and then the mixed alkoxide so formed, dimerises; this exothermic reaction can be represented by the following equations:

$$2M(OBu^{t})(OR)_{4} \rightarrow (RO)_{4}M \underbrace{O}_{O}M(OR)_{4} + heat$$

Bu^t

(R is Me or Et group)

It was further observed that tantalum penta-*tert*.-butoxide even after refluxing with ethanol for several hours gave tantalum mono-*tert*.-butoxide tetra-ethoxide.

REACTIONS OF TANTALUM PENTA-ETHOXIDE WITH ALCOHOLS IN BENZENE

$\overline{\frac{Ta(OEt)_5}{(g)}}$	Alcohol	Product, yield and state	b.p. (°C/mm)	Yield of distilled	Analy tantal	rsis of um
				product (%)	Foun (%)	d Calc. (%)
2.49	<i>n</i> -propanol (6.2 g)	Ta(OEt)(OPr ⁿ) ₄ (2.83 g); yellow liquid.	178/0.3	83	39.2	39.1
3.48	isopropanol (10.68 g)	Ta(OEt)(OPr ⁱ)4 (3.96 g); white, crystalline solid.	sublimes at 130–140/0.3	70	40.1	39. I
2.92	n-butanol (7.6g)	Ta(OEt)(OBu ⁿ)4 (3.72 g); yellow, viscous liquid.	199/0.1	96	34.7	34.9
2.47	<i>sec</i> butanol (9.6 g)	Ta(OBu*)5 (3.32 g); light-yellow liquid.	138/0.2	81	33.2	33.1
2.71	<i>tert.</i> -butanol (5.2 g)	Ta(OBu ^t)5* (3.67 g); white, crystalline solid.	sublimes at 90–100/0.3	67	33.9	33.1
3.28	<i>tert.</i> -pentanol (8.6 g)	Ta(OEt)(OAm ^t) ₄ (4.63 g); colourless, pasty solid.	148/0.3	60	31.1 ethoxy 6.8	31.5 ethoxy 7.8

* Contains 2.2% ethoxy in the sublimed product.

These results could be explained on the basis of increasing steric hindrance offered to intermolecular coordination by the increased ramification of the alkyl groups; the energetics of the reactions also appear to play an important role. It has already been reported that heat evolved in the interchange reactions of titanium zirconium tetra-tert.-butoxides with simpler alcohols follows the order MeOH \geq EtOH > Pr⁴OH. However, in the cases of niobium and tantalum penta-tert.-butoxides the difference between the reactivities of methanol, ethanol and isopropanol appear to be almost evened out.

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A lkoxide	Alcohol	Product, yield and state	b.p.	Yield of	Analysi	S		
			(^C(mm)	arstillea product	Found ((%)	Calc. (%	(9
				(%)	Nb	Alkoxy	Nb	Alkoxy
Nb(OMe)5 (1.72 g)	Bu ^t OH (2.55 g)	Nb(OBu ⁴) _{1.5} (OMe) _{3.5} (2.16 g); colourless, viscous liquid.	153/0.5	88	29.5	34.0	29.8	34.9
Nb(OEt)5 (2.65 g)	Bu ^t OH (3.05 g)	Nb(OBu')(OEt)4 (2.90 g); colourless, viscous liquid.	138/0.1	81	27.1	49.6	26.8	52.1
Nb(OPr ^{<i>i</i>}) ₅ (1.78 g)	Bu ^t OH (1.68 g)	Nb(OBt)(OPrt), (1.85 g); white, crystalline solid.	83/0.5	64	23.1	56.5	23.1	58.7
Nb(OBu ^t) ₅ (1.84 g)	MeOH (0.65 g)	Nb(OBu')(OMe)4 (1.16 g); colourless, viscous liquid.	163/0.8	89	32.1	41.3	32.0	42.8
Nb(OBu ^t) ₅ (1.59 g)	EtOH (o.80 g)	Nb(OBu ⁴)(OEt) ₄ (1.21 g); colourless, viscous liquid.	146/0.6	80	27.3	53.5	26.8	52.1
Nb(OBu ^t) ₅ (1.36 g)	Pr ⁱ OH (0.89 g)	Nb(OBu ^t)(OPr ^t) ₄ (1.18 g); white solid.	78/0.3	70	23.6	60.2	23,1	58.7

TABLE IV

REACTIONS OF T	ANTALUM PENT.	A-ALKOXIDES WITH ALCOHOLS IN MOLAR R	LATIO OF I:5 AT RC	OM TEMPERATUR	œ			
Alkoxides	Alcohol	Product, yield and state	b.p.	Yield of	Analysis			
			(\mathbf{v})	product	Found (°	(°)	Calc. (%)	
				(%)	Ta	Alkoxy	Ta	Alkoxy
Ta(OMe)5 (2.72 g)	Bu ^t OH (2.97 g)	Ta(OBu ^t) _{1.5} (OMe) _{3.5} (3.24 g); colourless, viscous liquid.	149/0.3	78	45.2	25.0	45.3	27.2
Ta(OEt)5 (2.18 g)	Bu ^t OH (1.96 g)	Ta(OBu ^t)(OEt) ₄ (2.32 g); colourless, viscous liquid.	163/8.0	83	43.3	40.7	41.7	41.5
Ta(OPr ⁱ)5 (3.36 g)	Bu ^t OH (2.58 g)	Ta(OBu¹)(OPr¹)₄ (3.46 g); white, crystalline solid.	sublimes at 90–95/0.6	60	37.2	50.3	36.9	48.2
Ta(OBu ^t) ₅ (2.00 g)	MeOH (o.59 g)	Ta(OBu ⁴)(OMe) ₄ (1.40 g); colourless, viscous liquid.	154/0.8	70	47.9	1	47.9	
Ta(OBu ^t) ₅ (1.93 g)	EtOH (o.81 g)	Ta(OBu ⁴)(OEt) ₄ (1.53 g); colourless, viscous liquid.	157/o.7	77	41.7	41.0	41.7	41.5
Ta(OBu ^t)5 (2.17 g)	EtOH (1.83 g) (reflux)	Ta(OBu ^t)(OEt) ₄ (1.53 g); colourless, viscous liquid.	146/0.2	varante	42.4	42.I	41.7	41.5
Ta(OBu ^t)5 (1.81 g)	Pr ⁱ OH (0.99 g)	Ta(OBut)(OPr ¹)4 (1.62 g); white, crystalline solid.	sublimcs at 95–100/0.4	61	36.3	47.7	36.9	48.2

TABLE V

EXPERIMENTAL

The apparatus and experimental techniques employed were similar to those already described16.

Reaction of niobium penta-ethoxide with tert.-butanol.

To a benzene (40 g) solution of niobium penta-ethoxide (2.31 g), tert.-butanol (8.9 g) was introduced. The reaction mixture were refluxed for about 6 h. The azeotrope (68°C) was first collected and it was further refluxed for about 40 h with slow fractionation. The remaining solvent was removed under reduced pressure, yielding a white solid (3.32 g).

Found: Nb, 23.7%; ethoxy, 6.2%.

On heating under reduced pressure, a white solid sublimed at 110-120°C/ 0.7 mm.

Found: Nb, 21.0%; ethoxy 2.4%. Calc. for Nb(OBu^t)₅: Nb, 20.3%.

Reaction between tantalum penta-tert.-butoxide and methanol (1:5) at room temperature.

An exothermic reaction occurred when methanol (0.59 g) was added to a solution of tantalum penta-tert.-butoxide (2.0 g) in benzene (4.0 g). It was retained overnight and the reaction mixture was dried under reduced pressure. A colourless, viscous liquid (1.40 g), distilling at 154°C/0.8 mm was obtained.

Found: Ta, 47.9%, Mol.wt. 781; Calc. for Ta(OBut)(OMe)4: Ta, 47.9%, Mol.wt. 378.

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