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Alkali-metal Hexa-alkoxides of Niobium and of Tantalum

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Reactions of niobium and tantalum penta-alkoxides with corresponding alkali-metal alkoxides have been studied and a number of double alkoxides of the type $MM'(OR)_6$ have been isolated (M = Li, Na, or K; M' = Nb or Ta; and R = Me, Et, Pr^i, or Bu^t). Tantalum derivatives can be purified by sublimation in a few cases whereas the niobium ones decompose to penta-alkoxides. Conductivities have been measured and molecular weights determined.

WITH aluminium,[1,2] titanium,[3] zirconium,[4] and uranium,[5] alkali-metal alkoxides form stable covalent double alkoxides. We find no reference to double alkoxides of niobium and tantalum. Gut,[6] however, deduced the presence of double alkoxides, $LiM'(OCH_3)_6$ in pH titrations of $M'Cl_5$ (M' = Nb or Ta) with $LiOCH_3$ in methanol, so we considered it of interest to synthesise the double alkoxides of these two elements.

During this work the reactions of niobium and tantalum penta-alkoxides (methoxides, ethoxides, isopropoxides, and t-butoxides) with corresponding alkali-metal alkoxides (lithium, sodium, and potassium) in parent alcohols have been carried out and the compounds of the type $MNb(OR)_6$ and $MTa(OR)_6$ isolated according to eqn. (1), (where M' = Nb or Ta; M = Li, Na, or K; and R = Me, Et, Pr^i, or Bu^t).

$$M'(OR)_5 + MOR \longrightarrow MM'(OR)_6 \qquad (1)$$

All these double alkoxides are white solids (except the light brown t-butoxides), soluble in parent alcohols (solubility decreases from Li to K). Only $NaNb(OEt)_6$, $NaTa(OEt)_6$, and $KNb(OPr^i)_6$ could be recrystallised from their alcoholic solution. On attempting to purify them by distillation or sublimation under reduced

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pressure the niobium derivatives tend to decompose to the corresponding niobium penta-alkoxides according to equation (2). However the tantalum double alkoxides

$$MNb(OR)_6 \longrightarrow MOR + Nb(OR)_5 \qquad (2)$$

appear to be much more stable to heat. The $MTa(OR)_6$ derivatives (M = Na or K, R = Me or Et) were stable

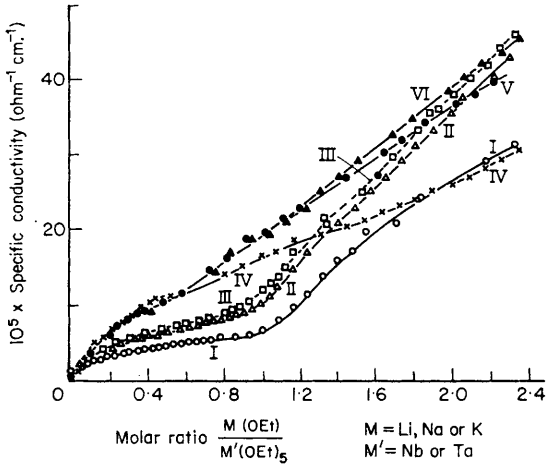

FIGURE 1 Titration between $M(OEt)_5$ and MOEt

I 0·019M-LiOEt against 0·122M-$Ta(OEt)_5$
II 0·020M-NaOEt against 0·122M-$Ta(OEt)_5$
III 0·020M-KOEt against 0·122M-$Ta(OEt)_5$
IV 0·019M-LiOEt against 0·104M-$Nb(OEt)_5$
V 0·020M-NaOEt against 0·104M-$Nb(OEt)_5$
VI 0·020M-KOEt against 0·104M-$Nb(OEt)_5$

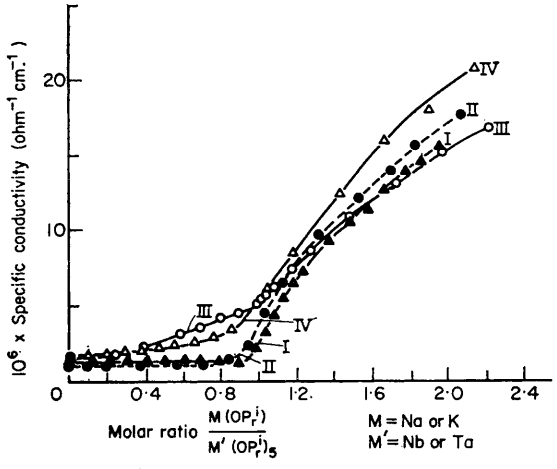

FIGURE 2 Titration between $M'(OPr^i)_5$ and $MOPr^i$

I 0·021M-$NaOPr^i$ against 0·107M-$Ta(OPr^i)_5$
II 0·020M-$KOPr^i$ against 0·107M-$Ta(OPr^i)_5$
III 0·021M-$NaOPr^i$ against 0·106M-$Nb(OPr^i)_5$
IV 0·020M-$KOPr^i$ against 0·105M-$Nb(OPr^i)_5$

to 320°/0·1 mm. [b.p.'s of $Ta(OMe)_5$ and $Ta(OEt)_5$ 189°/10 mm. and 202°/10 mm.]. The sodium and potassium derivatives of tantalum isopropoxide and t-butoxide appear to sublime under reduced pressure accompanied with some disproportionation. The thermal stability of these double alkoxides of tantalum appears to follow the orders Li > Na > K and OBu^t > OPr^i > OEt ~ OMe. Molecular weights and conductometric studies in the parent alcohol indicate that their relative extents of dissociation also appear to follow the order indicated above for thermal stability.

The reactions of $MNb(OEt)_6$ (M = Li or Na) with acetylacetone in molar ratio 1 : 1 in benzene gave compounds of the type $MNb(OEt)_5(acac)$ which decomposed on heating under reduced pressure to $Nb(OEt)_4(acac)$.

Molecular-weight determinations of these derivatives in the parent alcohol shows them to be slightly dissociated; the dissociation appears to be a maximum for methoxide derivatives, which may at least partly be ascribed to the higher dielectric constant of methanol. Similar observations have been reported by Bradley and his co-workers,[7,8] who found the molecular complexities of niobium and tantalum pentamethoxide in methanol to be 1·34 and 1·2 respectively, which are quite low compared with those of the ethoxide derivatives.

Conductometric titrations of niobium and tantalum penta-methoxides, -ethoxides, and -isopropoxides with alkali-metal alkoxides showed one sharp break in the case of tantalum penta-ethoxide and niobium and tantalum penta-isopropoxides (Figures 1 and 2) indicating the formation of $MM'(OR)_6$. No distinct point of inflexion could be detected in the corresponding titrations of methoxides and niobium pentaethoxide. The conductivity of niobium and tantalum penta-t-butoxides as well as alkali t-butoxides in t-butyl alcohol was too low to be measured with our equipment.

EXPERIMENTAL

Precautions were taken to exclude moisture and interchangeable standard joints were used throughout.

Niobium and tantalum penta-alkoxides were synthesised as reported.[7-9] Lithium, sodium, and potassium metals, (AnalaR) were weighed in a dry-box. Alcohols were dried as described previously.[10]

Molecular weights were determined with a Gallenkamp ebulliometer. The reactants were mixed, and the conductometric measurements made with a TESLA conductivity bridge, in a conductivity cell (constant 0·194) in a dry-box of very low humidity.

Niobium and tantalum were estimated as their pentoxides.[10] Alkoxy-groups were estimated by oxidation with N-potassium dichromate in 12·5% sulphuric acid.[11]

Reaction between Niobium Pentamethoxide and Sodium Methoxide in Molar Ratio 1 : 1 *in Methanol.*—Sodium (0·21 g.) was added to a suspension of niobium pentamethoxide (2·28 g.) in methanol (8 g.), causing an exothermic reaction. The solution became blue probably owing to initial reduction of Nb^V to Nb^{IV}; after a few minutes it became colourless. The contents were refluxed for ½ hr., cooled, and left overnight. After distilling off excess of methanol under re-

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duced pressure, a white solid (2·7 g.) was obtained which was sparingly soluble in benzene. When this (1·0 g.) was heated under reduced pressure, a few drops of yellow viscous liquid (0·4 g.) were obtained at 160°/0·8 mm. [Found: Nb, 37·8; MeO, 63·4. Calc. for $Nb(OMe)_5$: Nb, 37·4; MeO, 62·6%].

Reaction between Tantalum Pentaisopropoxide and Sodium Isopropoxide in Molar Ratio 1 : 1 *in Isopropyl Alcohol.*—To a solution in isopropyl alcohol (9·5 g.) of tantalum pentaisoproproxide (3·87 g.), sodium (0·258 g.) was added. It slowly dissolved at low temperature and the contents were refluxed for 1 hr. The clear colourless solution was allowed to cool and the solvent was distilled off first under ordinary pressure and then under reduced pressure. White crystals

TABLE 1

Reactions of niobium and tantalum penta-methoxides with alkali-metal methoxides in molar ratio 1 : 1 in methanol. All the products are white crystalline solids, soluble in methanol

Methoxide (g.)	Alkali-metal in methanol (g.)	Product and yield (g.)	Found (%) Metal	Found (%) OMe	Calc. (%) Metal	Calc. (%) OMe	Molecular weight Found	Molecular weight Calc.	Action of heat under reduced pressure
$Nb(OMe)_5$ 2·89	Lithium 0·08	$LiNb(OMe)_6$ 3·2	32·2	66·3	32·5	65·1	—	—	Disproportionates to $Nb(OMe)_5$
2·28	Sodium 0·21	$NaNb(OMe)_6$ 2·7	30·6	63·1	30·8	61·6	243	302	Disproportionates to $Nb(OMe)_5$
1·81	Potassium 0·28	$KNb(OMe)_6$ 2·3	29·7	60·2	29·2	58·5	206	318	Disproportionates to $Nb(OMe)_5$
$Ta(OMe)_5$ 2·94	Lithium 0·06	$LiTa(OMe)_6$ 3·2	49·0	51·6	48·4	49·8	—	—	A small amount of white solid corresponding in analysis to $LiTa(OMe)_6$ could be distilled out at 260°/0·1 mm.
2·60	Sodium 0·18	$NaTa(OMe)_6$ 3·0	47·2	49·5	46·4	47·7	213	390	Stable to 320°/0·1 mm.
1·90	Potassium 0·22	$KTa(OMe)_6$ 2·3	45·6	47·6	44·5	45·8	242	406	Stable to 320°/0·1 mm.

TABLE 2

Reactions of niobium and tantalum penta-ethoxides with alkali-metal ethoxides in molar ratio 1 : 1 in ethanol. All the products are white crystalline solids soluble in ethanol

Ethoxide (g.)	Alkali metal in ethanol (g.)	Product formed and yield (g.)	Found (%) Metal	Found (%) OEt	Calc. (%) Metal	Calc. (%) OEt	Molecular weight Found	Molecular weight Calc.	Action of heat under reduced pressure
$Nb(OEt)_5$ 2·12	Lithium 0·046	$LiNb(OEt)_6$ 2·40	25·6	72·2	25·1	73·0	—	—	Disproportionates to $Nb(OEt)_5$
2·40	Sodium 0·174	$NaNb(OEt)_6$ 2·9	24·1	70·8	24·0	70·0	332	386	Disproportionates to $Nb(OEt)_5$
2·59	Potassium 0·317	$KNb(OEt)_6$ 3·2	23·9	66·2	23·1	67·2	—	—	Disproportionates to $Nb(OEt)_5$
$Ta(OEt)_5$ 2·92	Lithium 0·05	$LiTa(OEt)_6$ 3·2	40·6	59·4	39·5	59·0	442	458	Deposited a small amount of white solid at 330°/0·2 mm. which corresponded in analysis to $LiTa(OEt)_6$
2·36	Sodium 0·13	* $NaTa(OEt)_6$ 2·6	39·1	56·8	38·2	56·9	444	474	Stable to 330°/0·2 mm.
2·24	Potassium 0·22	$KTa(OEt)_6$ 2·75	38·0	55·3	36·9	55·1	418	490	Stable to 330°/0·2 mm.

* Could be crystallised from ethanol solution.

TABLE 3

Reactions of niobium and tantalum penta-isopropoxides with alkali-metal isopropoxides in molar ratio 1 : 1 in isopropyl alcohol. All the products are white crystalline solids, soluble in isopropyl alcohol

Isopropoxide (g.)	Alkali-metal in isopropyl alcohol (g.)	Product formed and yield (g.)	Found (%) Metal	Found (%) OPr^i	Calc. (%) Metal	Calc. (%) OPr^i	Molecula weight Found	Molecula weight Calc.	Action of heat under reduced pressure
$Nb(OPr^i)_5$ 1·95	Lithium 0·035	$LiNb(OPr^i)_6$ 2·3	20·7	78·7	20·5	78·0	—	—	Stable to 140°/0·2 mm. then decomposes to give $Nb(OPr^i)_5$
1·68	Sodium 0·10	$NaNb(OPr^i)_6$ 2·0	19·5	75·3	19·7	75·3	—	—	Stable up to 200°/0·8 mm. then decomposes to give $Nb(OPr^i)_5$
1·35	Potassium 0·136	* $KNb(OPr^i)_6$ 1·60	19·6	72·1	19·2	72·9	442	486	—
$Ta(OPr^i)_5$ 1·85	Lithium 0·027	$LiTa(OPr^i)_6$ 2·21	34·5	66·5	33·4	65·5	514	542	Sublimes at 160—180°/0·1 mm. Ta, 35·8; Pr^iO, 66·0%
2·06	Sodium 0·10	$NaTa(OPr^i)_6$ 2·50	33·1	63·9	32·5	63·5	516	558	Sublimes at 200—210°/0·2 mm. Ta, 33·9, Pr^iO, 63·5%
2·17	Potassium 0·178	$KTa(OPr^i)_6$ 2·65	33·0	61·2	31·5	61·7	—	—	Sublimes at 210—220°/0·1 mm. Ta, 36·9, Pr^iO, 62·2%

* Could be crystallised from isopropyl alcohol.

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TABLE 4

Reactions of niobium and tantalum penta-t-butoxides with alkali-metal t-butoxides in molar ratio 1 : 1 in t-butyl alcohol. All the products are soluble in t-butyl alcohol

t-Butoxide (g.)	Alkali metal in t-butyl alcohol (g.)	Produced formed; yield and state (g.)	Found (%) Metal	Calc. (%) Metal	Molecular weight Found	Molecular weight Calc.	Action of heat under reduced pressure
$Nb(OBu^t)_5$ 2·04	Lithium 0·03	$LiNb(OBu^t)_6$ (2·4) White solid	18·2	17·3	435	538	Sublimed at 110—120°/0·1 mm. to $Nb(OBu^t)_5$
1·33	Sodium 0·069	$NaNb(OBu^t)_6$ (1·60) Light yellow solid	17·0	16·8	—	—	Sublimed at 110—120°/0·1 mm. to $Nb(OBu^t)_5$
1·25	Potassium 0·107	$KNb(OBu^t)_6$ (1·6) Light brown solid	17·0	16·3	—	—	Sublimed at 110—120°/0·1 mm. to $Nb(OBu^t)_5$
$Ta(OBu^t)_5$ 2·32	Lithium 0·03	$LiTa(OBu^t)_6$ (2·64) White solid	30·0	28·9	410	626	Sublimed at 110—120°/0·1 mm. to $LiTa(OBu^t)_6$, 31·2%
1·50	Sodium 0·063	$NaTa(OBu^t)_6$ (1·78) Light yellow solid	29·2	28·2	—	—	Sublimed at 110—120°/0·1 mm. to $NaTa(OBu^t)_6$, 30·9%
1·13	Potassium 0·081	$KTa(OBu^t)_6$ (1·31) Light brown solid	28·3	27·5	—	—	—

(4·79 g.) were obtained. On heating the crystalline solid (4·0 g.) under reduced pressure (0·3 mm.), white crystals (2·5 g.) were obtained.

Analyses of the above compounds and results of other reactions of niobium and tantalum alkoxides with alkali-metal alkoxides are summarised in Tables 1—4.

Reaction between $LiNb(OEt)_6$ *and Acetylacetone in Molar Ratio* 1 : 1.—An exothermic reaction occurred when acetylacetone (0·67 g.) was added to $LiNb(OEt)_6$ (2·46 g.). Benzene (40 g.) was added giving a white turbid solution. It was refluxed under a fractionating column with slow fractionation of ethanol–benzene azeotrope. After removing the excess of solvent under reduced pressure, a yellow solid (2·8 g.) was obtained [Found: Nb, 22·6%; ethanol in azeotrope, 0·33 g. Calc. for $NaNb(OEt)_5(acac)$: Nb, 21·9%; ethanol, 0·31 g.].

When the above compound (2·3 g.) was heated at 127°/1·0 mm. an orange-yellow viscous liquid (1·6 g.) was obtained which solidified as an orange-yellow solid [Found: Nb, 25·2. Calc. for $Nb(OEt)_4(acac)$: Nb, 24·95%].

Reaction between $NaNb(OEt)_6$ *and Acetylacetone in Molar Ratio* 1 : 1.—Acetylacetone (0·42 g.) was added as above to a benzene solution of $NaNb(OEt)_6$ (1·6 g.), causing an exothermic reaction. After removal of the excess of solvent, a brown yellow solid (2·4 g.) was obtained, which disproportionated on being heated under reduced pressure to $Nb(OEt)_4(acac)$ [Found: Nb, 22·0%; ethanol in azeotrope, 0·21 g. Calc. for $NaNb(OEt)_5(acac)$: Nb, 21·1%; ethanol, 0·19 g.].

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