854. *Structural Chemistry of the Alkoxides. Part VIII.* Isomeric Butoxides and Pentyloxides of Niobium.*

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The isomeric butoxides and pentyloxides (excepting the *tert.*-alkoxides) of niobium have been prepared and their molecular weights in boiling benzene and their volatilities have been determined. The physicochemical properties of the niobium alkoxides are compared with those of the corresponding tantalum derivatives. In contrast to tantalum, which forms stable penta-*tert.*-alkoxides, niobium gives oxy-derivatives with tertiary alkoxides and no penta-*tert.*-alkoxides of niobium could be isolated. This difference is discussed from the theoretical standpoint and is related to the lower thermal stability of *n*-alkoxides of niobium.

THE preparation and properties of *n*-alkoxides of niobium[1] and of tantalum[2] and the isomeric butoxides and pentyloxides of tantalum[3] have recently been described. We now describe the isomeric butoxides and pentyloxides of niobium and make an extensive comparison between the alkoxides of niobium and of tantalum. A feature of the *n*-alkoxides was the variation in relative volatility of niobium and tantalum compounds with the chain length of the alkyl group and it was of interest to gain further information for branched-chain derivatives. It was also noteworthy that niobium *n*-alkoxides seemed less stable thermally than the tantalum derivatives, presumably owing to electronic factors, and it was expected that this contrast in behaviour would be affected by the enhanced inductive effects of branched-chain alkyl groups.

The new alkoxides of niobium were prepared either from the pentachloride by the ammonia method[1] or by alcohol interchange on the pentaethoxide.[1] The molecular weights were determined ebullioscopically in benzene, and boiling points were measured at pressures near 0·1 mm. The low thermal stability of the alkoxides precluded measurements at higher pressures.

Isomeric Butoxides.—The molecular complexities and boiling points of the isomeric butoxides of niobium and tantalum are presented in Table 1, in which a striking feature is the absence of niobium *tert.*-butoxide. In spite of several variations in preparative procedure we have not been able to isolate a penta-*tert.*-butoxide, the products always being oxide *tert.*-butoxides such as $Nb_2O(OBu^t)_8$ and $NbO(OBu^t)_3$. For the present we assume that the penta-*tert.*-butoxide, if it exists, is insufficiently stable to survive normal preparative procedure. On the other hand, tantalum forms a relatively stable penta-*tert.*-butoxide which may be distilled unchanged[3] at 5·5 mm., and this behaviour of the *tert.*-butoxides appears to constitute a major chemical difference between niobium and tantalum and will be further discussed under the isomeric pentyloxides. Another feature of Table 1 is that the b. p. of the niobium butoxide is invariably lower than that of the corresponding tantalum derivative. These are further examples of volatile compounds which may be suitable for the separation of niobium from tantalum by distillation. A similarity between niobium and tantalum is reflected in the parallel increase in volatility with increased

TABLE 1.

	B. p./0·1 mm.		Mol. complexity	
R in $M(OR)_5$	Nb	Ta	Nb	Ta
$Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$	195°	215°	2·01	2·02
$Me_2CH{\cdot}CH_2$	160 *	185 †	1·83	2·04
MeEtCH	112·5	137·5	1·14	1·06
Me_3C	—	96 ‡	—	1·00

* M. p. 150°. † M. p. 157°. ‡ Temp. of sublimation.

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* Part VII, *J.*, 1956, 3469.

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

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

[3] *Idem, ibid.*, 1956, 1139.

branching of the butyl group coupled with a corresponding decrease in molecular complexity. In each case the greatest change occurs in passing from *iso*butoxide to *sec.*-butoxide. However, the molecular complexity of niobium *sec.*-butoxide appears anomalously high. A further similarity is in the crystalline nature of the *iso*butoxides which are close in melting point.

Isomeric Pentyloxides.—The data on these oxides are given in Table 2. The pentyloxides of niobium resemble the tantalum derivatives in showing the expected variation of volatility and molecular complexity with branching of the pentyl group. In each case there is a marked change in passing from the derivative of 2-methylbutan-1-ol (*sec.*-butylcarbinol) to the *neo*pentyloxide which suggests that stereochemical factors are primarily responsible for the change. Both *neo*pentyloxides are anomalous in exhibiting greater molecular complexities but lower b. p.s than the secondary pentyloxides and this is probably related to the high m. p.s of the *neo*pentyloxides (cf. ref. 3). A further anomaly is the higher complexity of the niobium derivative of pentan-3-ol (diethylcarbinol) compared with the tantalum compound and this recalls the behaviour of the *sec.*-butoxides (Table 1). The differences in b. p. (ΔT = b. p. of Ta compd. — b. p. of Nb compd.) are also shown in Table 2, and it is noticeable that niobium alkoxides are closer in b. p. to the corresponding tantalum compounds in the pentyloxides than in the butoxides. The most interesting feature of the pentyloxides is the apparent non-existence of niobium penta-*tert.*-amyloxide. Attempts to obtain this compound under the mildest conditions always produced an oxide *tert.*-amyloxide. Moreover, a similar result was obtained with 3-ethylpentan-3-ol (triethylcarbinol) and it appears that penta-*tert.*-alkoxides of niobium are unstable and break down to oxy-compounds in contrast to the stability of the corresponding tantalum derivatives. This calls to mind the behaviour of the complex fluorides, *e.g.*, $K_2[MF_7]$, in which the niobium compound readily passes into the more stable oxyfluoroniobate $K_2[NbOF_5]$, and also the fact that in general niobium has a much stronger tendency than tantalum to form oxy-compounds. In connection with the *n*-alkoxides of niobium and tantalum[1] we have already suggested that the tendency of niobium to form oxy-compounds promotes the release of a carbonium ion from a Nb–O–C system, *viz.*:

TABLE 2.

	B. p./0·1 mm.			Mol. complexity	
R in $M(OR)_5$	Nb	Ta	ΔT	Nb	Ta
$Me{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$	228°	233°	5·0°	2·00	2·01
$Me_2CH{\cdot}CH_2{\cdot}CH_2$	199	210	11·0	1·81	1·98
$MeEtCH{\cdot}CH_2$	183	204	21·0	1·81	1·97
$Me_3C{\cdot}CH_2$	126 *	130 †	4·0	1·52	1·35
Et_2CH	138	153	15·0	1·16	1·02
$MePr^nCH$	137·5	148	10·5	1·03	0·99
$MePr^iCH$	139	137	−2·0	1·05	1·02
$MeEt_2C$	—	139	—	—	1·00

* M. p. 90°. † M. p. 120°.

$$^{-}\mathrm{Nb}{=}{}^{+}\mathrm{OR} \longrightarrow {}^{-}\mathrm{Nb}{=}\mathrm{O} + \mathrm{R}^{+}$$

The behaviour of the niobium *tert.*-alkoxides is consistent with this view because of the enhanced tendency of the *tert.*-alkyl group to assume the carbonium structure. Thus it is expected that the stability of a niobium alkoxide will be decreased by alkyl groups having pronounced $+I$ inductive effects. With this idea in mind we attempted to prepare the niobium derivative of 1-phenylethanol which should behave like a secondary alcohol with a strong $+I$ effect. Under mild conditions the penta-(1-phenylethoxide) of niobium was obtained as a material which decomposed when heated. It is clear that a detailed investigation is required to explain fully this interesting behaviour of niobium *tert.*-alkoxides, but our experiments show that electronic factors rather than stereochemical factors are responsible. The possibility of utilising this contrast between niobium and tantalum for separating these elements is now being investigated, but it is also feasible that the niobium oxide *tert.*-alkoxides may act as catalysts for the breakdown of the more stable *tert.*-alkoxides of tantalum and thus prevent easy separation.

EXPERIMENTAL

The general experimental details are the same as those reported previously.[1]

*Niobium Penta*iso*butoxide.*—Niobium pentachloride (7·9 g.), suspended in benzene (200 c.c.), was treated with *iso*butyl alcohol (50 c.c.) and then excess of ammonia. After removal of ammonium chloride by filtration the filtrate was evaporated to dryness and gave a grey chloride-free solid (12·65 g.) which was recrystallised from *iso*butyl alcohol (100 c.c.). After five crystallisations a pure white solid (8·6 g.) was obtained [Found: Nb, 20·2. $Nb(OC_4H_9)_5$ requires Nb, 20·3%].

Niobium Penta-(1-methylpropoxide).—The new *alkoxide* was obtained as a pale yellow liquid (13·8 g.) from the reaction involving the pentachloride (9·9 g.), *sec.*-butyl alcohol (50 c.c.), and excess of ammonia in benzene (200 c.c.). Distillation (98·5°/0·02 mm.) gave a chloride-free liquid (11·9 g.) (Found: Nb, 20·2%).

*Niobium Penta-*tert.*-butoxide.*—(*a*) The reaction involving the pentachloride (6·7 g.) suspended in light petroleum (b. p. 40—60°, 200 c.c.) with *tert.*-butyl alcohol (50 c.c.) and excess of ammonia gave a dark, chloride-free solid (7·5 g.) [Found: Nb, 28·1. $NbO(OC_4H_9)_3$ requires Nb, 28·3%].

(*b*) The pentachloride (4·6 g.) was added to pyridine (125 c.c.) and after the addition of *tert.*-butyl alcohol (50 c.c.) the mixture was treated with excess of ammonia. After removal of ammonium chloride by filtration the filtrate was evaporated to dryness. The product was dissolved in benzene (200 c.c.) and treated with *tert.*-butyl alcohol (10 c.c.) and ammonia. A further amount of ammonium chloride was filtered off and the filtrate when taken to dryness gave a black solid (Found: Nb, 25·4; Cl, 2·2%). Pyridine was used in expt. (*b*) to avoid possible side reactions between hydrogen chloride and the tertiary alcohol leading to the formation of water which could have occurred in expt. (*a*).

(*c*) With the utmost precautions to prevent hydrolysis the pentachloride (7·9 g.) in pyridine (100 c.c.) was mixed with ice-cold benzene–*tert.*-butyl alcohol azeotrope and then treated with ammonia twice as in expt. (*b*). The final black solid product (9·75 g.) was not the pentabutoxide (Found: Nb, 22·5; Cl, 2·2%). In another similar experiment a dark chloride-free *product* was obtained [Found: Nb, 23·7. $Nb_2O(Bu)_8$ requires Nb, 23·6%]. Another experiment involving the reaction between the pentachloride and sodium *tert.*-butoxide in benzene also failed to yield the penta-*tert.*-butoxide.

*Niobium Penta*iso*pentyloxide.*—*iso*Pentyl alcohol (42 g.) was added dropwise to the pentachloride (6·9 g.) suspended in benzene (200 c.c.), and the solution treated with excess of ammonia. The new *alkoxide*, isolated in the usual manner, was distilled (206°/0·2 mm., some decomp.) and gave a red, chloride-free distillate [Found: Nb, 18·1. $Nb(OC_5H_{11})_5$ requires Nb, 17·6%].

Niobium Penta-(2-methylbutoxide).—The pentachloride (5·9 g.), 2-methylbutan-1-ol (30 g.), and ammonia were allowed to react in benzene (200 c.c.) in the foregoing manner and the new *alkoxide* was isolated as a viscous red liquid and then distilled (169°/0·02 mm.) (Found: Nb, 17·9%).

*Niobium Penta*neo*pentyloxide.*—*neo*Pentyl alcohol (12·3 g.) was caused to react with niobium pentaethoxide (5·9 g.) in benzene (100 c.c.), and the ethyl alcohol removed as the binary azeotrope with benzene. After evaporation of the benzene the solid product was heated at 100°/0·1 mm. for several hours to remove excess of *neo*pentyl alcohol (Found: Nb, 17·6%).

Niobium Penta-(1-ethylpropoxide).—Ice-cold pentan-3-ol (diethylcarbinol) (42 g.) was added dropwise to a suspension of the pentachloride (7·0 g.) in frozen benzene (200 c.c.) and the mixture was treated with excess ammonia. The new *alkoxide* was isolated in the usual manner as a red viscous liquid which was distilled (138°/0·1 mm.) and gave a red, chloride-free gelatinous distillate (11·9 g.) (Found: Nb, 17·5%).

Niobium Penta-(1-methylbutoxide).—The pentachloride (8·05 g.), suspended in pyridine (144 g.),. was treated with pentan-2-ol (44 g.) and then excess of ammonia. The product remaining after removal of ammonium chloride and solvent was dissolved in benzene and again treated with ammonia and the alcohol. The new *alkoxide* was then isolated as a red liquid which was distilled (123·5°/0·02 mm.) and gave a red chloride-free product (6·84 g.) (Found: Nb, 17·5%).

Niobium Penta-(1 : 2-dimethylpropoxide).—The new *alkoxide* (10 g.) was isolated in the foregoing manner as a pale yellow distillate (b. p. 125°/0·02 mm.) from the reaction involving the pentachloride (5·2 g.), 2-methylbutan-3-ol (methyl*iso*propylcarbinol) (51·8 g.), pyridine (150 c.c.), and ammonia (Found: Nb, 17·6%).

Niobium Penta-(1 : 1-dimethylpropoxide).—(*a*) The pentachloride (9·9 g.) in pyridine (108 g.)

was allowed to react with *tert.*-amyl alcohol (35·8 g.) and excess of ammonia. The viscous product isolated in the usual manner decomposed completely when distillation was attempted (160°/0·7 mm.). (*b*) In another experiment involving the pentachloride (5·38 g.), pyridine (175 c.c.), *tert.*-amyl alcohol (36·4 g.), and ammonia, a dark viscous product (9·8 g.) was isolated at room temperature [Found: Nb, 20·0. $Nb_2O(OC_5H_{11})_8$ requires Nb, 20·7%]. This *product* decomposed during sublimation (120°/0·1 mm.). (Sublimate. Found: Nb, 27·4%.)

Molecular Weights.—These were determined ebullioscopically in benzene by the usual method[1] and the results are given in Table 3.

TABLE 3

R in $Nb(OR)_5$	Range of *m* (g.)	Benzene (g.)	$\Delta T/m$	*M*	
				Found	Calc.
$Me_2CH{\cdot}CH_2$	0·0108—0·1262	15·18	0·231°	840	457·9
MeEtCH	0·0099—0·0500	15·27	0·366	526	,,
$Me_2CH{\cdot}CH_2{\cdot}CH_2$	0·0311—0·1470	13·50	0·228	953	527·9
$MeEtCH{\cdot}CH_2$	0·0426—0·2136	15·07	0·200	954	,,
$Me_3C{\cdot}CH_2$	0·0150—0·0582	15·76	0·232	804	,,
Et_2CH	0·0365—0·1492	15·25	0·315	612	,,
$MePr^nCH$	0·0164—0·0844	14·71	0·366	546	,,
$MePr^iCH$	0·0095—0·0476	15·28	0·346	555	,,

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