460. *Normal Alkoxides of Quinquevalent Niobium.*

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The new alkoxides $Nb(OR)_5$, where R = Me, Et, Pr^n, Bu^n, or *n*-pentyl, have been prepared by reactions involving niobium pentachloride, the alcohol, and ammonia, or by alcohol-interchange involving niobium pentaethoxide. Boiling points under reduced pressure and ebullioscopic molecular weights in benzene, in toluene, and in the parent alcohols were determined. The niobium *n*-alkoxides are less stable than the corresponding tantalum compounds. The volatilities and molecular complexities of the niobium and tantalum *n*-alkoxides are discussed from the theoretical viewpoint.

THE preparation and properties of some tantalum penta-*n*-alkoxides have recently been described.[1] In view of the chemical similarity between niobium and tantalum it seemed worthwhile to investigate the alkoxides of niobium. Additional interest was centred on the relative volatilities of corresponding niobium and tantalum alkoxides because of the possibility that the effect of molecular weight on volatility [2] might be apparent. This communication deals with the *n*-alkoxides $Nb(OR)_5$, where R = Me, Et, Pr^n, Bu^n, and *n*-pentyl.

These compounds may be prepared by either of the methods :

$$NbCl_5 + 5NH_3 + 5ROH \longrightarrow Nb(OR)_5 + 5NH_4Cl$$
$$Nb(OEt)_5 + 5ROH \longrightarrow Nb(OR)_5 + 5EtOH$$

Niobium pentamethoxide is a white crystalline solid, m. p. 60° [cf. $Ta(OMe)_5$, m. p. 50°], but the other *n*-alkoxides are pale yellow liquids. The ease of hydrolysis in water appears to parallel the water-miscibility of the parent alcohols. A notable feature of the niobium *n*-alkoxides is the decrease in thermal stability with increase in length of the alkyl chain in contrast to the behaviour of the corresponding *n*-alkoxides of tantalum. Thus distillation of niobium *n*-pentyloxide causes decomposition even at 0·1 mm. whereas tantalum *n*-pentyloxide boils unchanged at a higher temperature. The boiling points of niobium and tantalum *n*-alkoxides under reduced pressure are presented in the Table : their main feature is the dependence on the length of the alkyl chain. As shown in the Figure the methoxides and ethoxides of tantalum are more volatile than the niobium derivatives whilst for the higher *n*-alkoxides the reverse is the case; this applies to both the pressure ranges investigated. These results also suggest that the separation of niobium and tantalum by distillation of the alkoxides (now being investigated) should be relatively simple.

	Boiling point (°/mm.)			
	Lower pressure		Higher pressure	
R in $M(OR)_5$	Nb	Ta	Nb	Ta
Me	153°/0·1	130°/0·2	200°/5·5	189°/10
Et	156°/0·05	146°/0·15	207°/5·5	202°/10
Pr^n	166°/0·05	184°/0·15	218°/5·5	232°/10
Bu^n	197°/0·15	217°/0·15	230°/5·5	256°/10
n-Pentyl	223°/0·15	239°/0·2	—	—

The molecular weights of the niobium *n*-alkoxides were determined ebullioscopically in benzene, in toluene, and in the parent alcohols, and the molecular complexities are tabulated

	Molecular complexity					
	In benzene		In toluene		In ROH	
R in $M(OR)_5$	Nb	Ta	Nb	Ta	Nb	Ta
Me	2·11	1·98	1·90	1·83	1·34	1·20
Et	2·02	1·98	1·89	1·83	1·52	1·78
Pr^n	2·02	1·95	1·79	1·83	1·29	1·70
Bu^n	2·01	2·02	1·74	1·83	1·13	1·40
n-Pentyl	2·00	2·01	—	—	—	—

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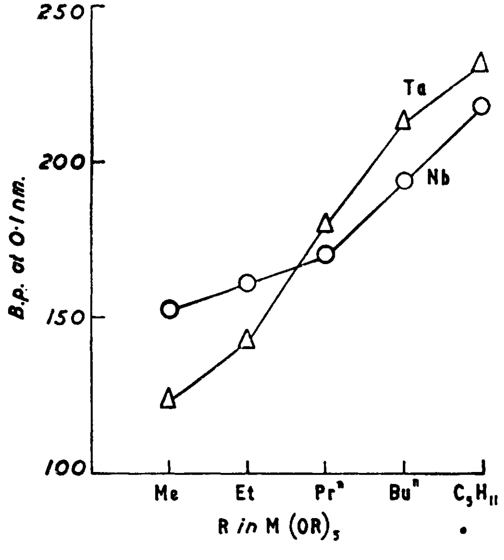
[1] Bradley, Wardlaw, and Whitley, *J.*, 1955, 726.

[2] Bradley, *Nature*, 1954, **174**, 323.

together with the data for the corresponding tantalum alkoxides. The niobium and tantalum *n*-alkoxides are all dimeric in boiling benzene and it seems likely that these metals are both 6-co-ordinate (see Figure in ref. 1). Dissociation of the dimers at a higher temperature is apparent from the results in boiling toluene. However, whilst the tantalum *n*-alkoxides all have the same complexity, there is a distinct decrease in complexity in toluene with increase in chain length for the niobium compounds. We infer that the energy of depolymerisation is sensibly constant for the tantalum series but decreases with increase in chain length for the niobium *n*-alkoxides. This is qualitatively consistent with the dependence of relative volatility of niobium and tantalum *n*-alkoxides on chain length. Thus the energy of polymerisation will be included in the molar heat of vaporisation, *i.e.*, $L_v = L_{mon.} + E$, where L_v = molar heat of vaporisation, $L_{mon.}$ = hypothetical heat of vaporisation of " monomeric " alkoxide,[3] and E = energy of depolymerisation. It seems reasonable to assume that $L_{mon.}$ for a niobium alkoxide will be close to that for the corresponding tantalum compound (cf. hafnium and zirconium alkoxides [4]), and differences in E will therefore be reflected as differences in L_v. If E for $Nb(OMe)_5$ exceeds E for $Ta(OMe)_5$ then according to the view that E for tantalum *n*-alkoxides is constant whilst for niobium *n*-alkoxides it varies in the order, methoxide > ethoxide > *n*-propoxide > *n*-butoxide > *n*-pentyloxide; it seems possible that the relative values of L_v will be: $Nb(OMe)_5 > Ta(OMe)_5$; $Nb(OEt)_5 > Ta(OEt)_5$; and $Nb(OR)_5 < Ta(OR)_5$, where R = Prⁿ, Buⁿ, or *n*-pentyl. This postulated order of L_v's is in agreement with the order of boiling points given above. Some support for this argument is forthcoming from the complexities of the alkoxides in their parent alcohols (see Table). It has been suggested [5] that the primary factors causing dissociation of tantalum *n*-alkoxides in their boiling parent alcohols are (1) the boiling point of the solvent (temperature effect) and (2) the " donor " power of the solvent (solvation effect). The same arguments must apply to niobium alkoxides and hence it is deduced that $E_{Nb(OMe)_5} > E_{Ta(OMe)_5}$ and $E_{Nb(OR)_5} < E_{Ta(OR)_5}$, where R = Et, Prⁿ, or Buⁿ. Only with the ethoxides does the order of E's conflict with that suggested above for L_v's. It is clear that vapour pressures (on which work is in progress) will give valuable information concerning these phenomena.



Since the atomic radii of niobium and tantalum are the same (1·34 Å) these differences in the behaviour of their alkoxides must be ascribed to electronic factors. It is well known that niobium differs from tantalum in having a pronounced tendency to form oxy-compounds containing the niobium–oxygen double bond and hence there will be a greater tendency for covalency expansion involving " intramolecular " bonding as in $(RO)_4\overset{-}{Nb}=\overset{+}{O}R$ to compete with the intermolecular bonding which causes dimerisation. This will lead to a readier depolymerisation with increase in temperature for the niobium compounds than for the tantalum derivatives. This easy double bonding between niobium and oxygen may also explain the lower thermal stability of the niobium alkoxides which will tend to split off carbonium ions, *viz.*, $Nb(OR)_5 \longrightarrow (RO)_4\overset{-}{Nb}=O + R^+$. This mechanism will be enhanced by the $(+I)$ electron-releasing tendency of the alkyl group and

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[3] Bradley, Mehrotra, Swanwick, and Wardlaw, *J.*, 1953, 2025.
[4] Bradley, Mehrotra, and Wardlaw, *J.*, 1953, 1634.
[5] Bradley, Wardlaw, and Whitley, *J.*, 1956, 1139.

is in accord with the observed decrease in stability of niobium *n*-alkoxides with increase in chain length of the alkyl group.

According to current views on the effect of molecular weight on volatility [2] there should be a tendency for the heavier tantalum alkoxides to be more volatile than the corresponding niobium compounds although this effect is usually obscured by the differences in molar heats of vaporisation. However, we have already pointed out that the molecular complexities of the ethoxides in ethyl alcohol imply that E for $Ta(OEt)_5$ should exceed E for $Nb(OEt)_5$, and hence L_v for $Ta(OEt)_5$ should exceed L_v for $Nb(OEt)_5$ which would predict the order of volatilities, $Nb(OEt)_5 > Ta(OEt)_5$. The reverse order of volatilities observed might well be due to over-ruling of the unfavourable order of latent heats by the "mass effect." This problem should be resolved when vapour pressures are available.

EXPERIMENTAL

The experimental technique was essentially that used in previous work on metal alkoxides.[1, 3] Niobium was precipitated as the hydroxide, from a nitric acid solution of the sample, by means of dilute aqueous ammonia. After being washed with ammonium nitrate (5% solution) the precipitate was ignited to Nb_2O_5.

Preparation of Niobium Pentachloride.—Hecht and Schlappmann [6] showed that niobium pentoxide and thionyl chloride at 200° in a sealed tube give niobium pentachloride and sulphur dioxide. Their method is not convenient in the laboratory on the large scale but we found that the reaction proceeds under normal reflux of thionyl chloride when the latter is present in large excess. Our starting material was potassium oxyfluoroniobate $K_2[NbOF_5],H_2O$ prepared from tantalum-free ($<0{\cdot}5\%$ of Ta) niobium pentoxide. The following is a typical preparation: Niobium hydroxide, obtained by addition of dilute aqueous ammonia to the complex fluoride (20 g.) dissolved in water (500 c.c.), was well washed first with water then with absolute alcohol. Thionyl chloride (1 kg.) was added, slowly at first to moderate the reaction, and the mixture refluxed for 10—12 days. After removal of excess of thionyl chloride the crude niobium pentachloride (25 g.) (Found: Nb, 23·7; Cl, 53·3%) was sublimed at 150—250° in a current of dry nitrogen, and the sublimate was crystallised from carbon tetrachloride. The yellow crystalline solid (14·5 g.) (Found: Nb, 34·0; Cl, 62·6. Calc. for $NbCl_5$: Nb, 34·35; Cl, 65·65%) was suitable for the preparation of alkoxides.

Niobium Pentamethoxide.—Methyl alcohol (200 c.c.) was added to the pentachloride (8·2 g.) suspended in benzene (200 c.c.) and, after the cessation of the vigorous reaction, ammonia was passed in until in excess. After removal of ammonium chloride by filtration the filtrate was evaporated to leave a yellow oil (7·1 g.), which contained no chloride. Distillation (153°/0·1 mm.) afforded colourless *pentamethoxide* which solidified (6·2 g.), m. p. 60° [Found: Nb, 37·5; MeO, 61·4. $Nb(OMe)_5$ requires Nb, 37·5; MeO, 62·5%].

Niobium Pentaethoxide.—From the reaction involving the pentachloride (5 g.), ethyl alcohol (20 c.c.), and excess of ammonia in benzene (150 c.c.), the *pentaethoxide* was finally obtained as a yellow distillate (6·2 g.) [Found: Nb, 29·0; EtO, 70·0. $Nb(OEt)_5$ requires Nb, 29·2; EtO, 70·8%]. The yellow colour persisted during further distillation and a highly purified pentaethoxide was obtained as follows: The distillate (45 g.) from a similar preparation was converted into the crystalline mixed ethoxide-*iso*propoxide [$Nb(OEt)(OPr^i)_4$ and $Nb(OEt)_2(OPr^i)_3$] by treatment with boiling *iso*propyl alcohol (200 c.c.). Four further recrystallisations gave a colourless crystalline product which was converted into niobium pentaethoxide by four successive treatments with ethyl alcohol (200 c.c.). Distillation (156°/0·05 mm.) gave a faintly yellow liquid (25 g.) (Found: Nb, 29·3; EtO, 70·3%).

Niobium Penta-n-*propoxide.*—The *propoxide* was obtained as a pale yellow distillate (9·9 g.; b. p. 166°/0·05 mm.) after carrying out the reaction between the pentachloride (9·6 g.), *n*-propyl alcohol (30 c.c.), and excess of ammonia in benzene (250 c.c.) in the usual manner [Found: Nb, 23·9. $Nb(OC_3H_7)_5$ requires Nb, 23·9%].

Niobium Penta-n-*butoxide.*—Purified niobium pentaethoxide (5·1 g.) was converted into the butoxide by the addition of *n*-butyl alcohol (50 c.c.) and benzene (100 c.c.) and by removing the liberated ethyl alcohol by azeotropic distillation. After evaporation of benzene and excess of butyl alcohol the *pentabutoxide* was obtained as a pale yellow distillate (6·75 g.), b. p. 197°/0·15 mm., which was slow in reacting with water [Found: Nb, 20·3. $Nb(OBu^n)_5$ requires Nb, 20·3%]. Distillation at 5·5 mm. (under oxygen-free nitrogen) caused rapid darkening.

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[6] Hecht and Schlappmann, *Z. anorg Chem.*, 1947, **254**, 255.

Niobium Penta-n-*pentyloxide*.—The *pentyloxide* (3·75 g.) was obtained by alcohol interchange involving the pure ethoxide (3·05 g.) and pentyl alcohol (18·5 g.) in benzene. The distilled product, b. p. 223°/0·15 mm. [Found : Nb, 17·0. $Nb(OC_5H_{11})_5$ requires Nb, 17·6%], was water-repellent and was slowly hydrolysed by dilute nitric acid. Attempts to distil the compound at 5·5 mm. caused decomposition.

Molecular-weight Determinations.—The modified Menzies–Wright ebulliometer [7] was used. The internal-calibration method [5] with fluorene was employed as a check on the usual method.[1, 3] Typical results from the latter method are tabulated first, followed by those from the internal-calibration method.

				M	
Alkoxide	Range of *m* (g.)	Solvent (g.)	$\Delta T/m$	Found	Calc.
$Nb(OMe)_5$	0·0334—0·1455	17·20 [a]	0·326	524	247·9
,, ...	0·0395—0·2351	14·17 [b]	0·147	332	,,
$Nb(OEt)_5$	0·0769—0·2295	16·61 [a]	0·275	644	317·9
,, ...	0·0572—0·3928	13·94 [c]	0·168	483	,,
$Nb(OPr^n)_5$	0·0264—0·1219	14·40 [a]	0·260	785	387·9
,, ...	0·0176—0·0998	14·06 [d]	0·184	499	,,
$Nb(OBu^n)_5$	0·0179—0·0887	14·87 [a]	0·214	923	457·9
,, ...	0·030—0·1549	13·06 [e]	148·5 *	519	,,
$Nb(OC_5H_{11})_5$	0·0092—0·0350	15·34 [a]	0·182	1054	527·9

[a] Benzene; [b] methyl alcohol; [c] ethyl alcohol; [d] *n*-propyl alcohol; [e] *n*-butyl alcohol.
* B. p. elevation in mm. of water-pressure difference in the water-thermometer.

	Slope (mm./g. of solute)				
	Alkoxide		Fluorene		
Alkoxide	Range of *m* (g.)	Slope	Range of *m* (g.)	Slope	*M* in toluene, found
$Nb(OMe)_5$	0·0211—0·1128	247	0·0082—0·0535	701	472
$Nb(OEt)_5$	0·0259—0·1321	213	0·0242—0·0467	768	600
$Nb(OPr^n)_5$	0·0187—0·1178	178	0·0144—0·0371	747	696
$Nb(OBu^n)_5$	0·0431—0·1422	161	0·0200—0·0692	772	796

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[7] Bradley, Gaze, and Wardlaw, *J.*, 1955, 3977.