Reactions of Liquid Sodium with Transition-metal Oxides. Part VII.[1] The Oxides of Niobium and Tantalum

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The reactions of the oxides Nb_2O_5, NbO_2, NbO, and Ta_2O_5 with liquid sodium have been studied at 400 and 600 °C and the products examined by *X*-ray powder crystallography. In each case in which reaction took place the equilibrium products were found to be the transition metal together with the cubic form of Na_3NbO_4 or Na_3TaO_4. The possible reaction mechanisms of the oxides in liquid sodium are discussed. The reactions of the ternary oxides $NaNbO_3$, $NaTaO_3$, Na_3NbO_4, and Na_3TaO_4 with pure liquid sodium, and $NaTaO_3$ and Na_3TaO_4 with oxygen-doped liquid sodium, have all been studied.

THIS work is part of a programme of research into the behaviour of transition metals and their oxides with the liquid alkali metals. Some early work on the reaction of niobium pentoxide with liquid sodium has been reported [2] but application of the Phase Rule indicates that equilibrium had not been reached. A much more detailed study has been completed on the reactions of niobium oxides with liquid potassium [3] and comparisons can be drawn between the behaviour of these alkali metals with the niobium oxides. Studies of the corrosion of niobium and tantalum in liquid sodium [4] have shown that oxygen impurities play the dominant role. Similar effects are observed in the reactions of the oxides with liquid sodium, a consequence of this being that equilibrium is not readily attained in these reactions. The reactions of the niobium oxides with liquid potassium were found to attain equilibrium much more readily than was found with liquid sodium; the results of the liquid potassium reactions can therefore be used as a model for the reactions carried out in liquid sodium. Potassium was found to be capable of reducing niobium oxides to niobium metal with the formation of the ternary oxide K_3NbO_4; it is the formation of this ternary oxide which is, in fact, responsible for reduction. Similar behaviour will be described in this paper for the reactions of the niobium oxides, and tantalum pentoxide, with liquid sodium.

Ternary oxide formation was observed [4] on the surface of niobium and tantalum metal plates after immersion in liquid sodium containing dissolved oxygen. Metal

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[1] Part VI, M. G. Barker and A. J. Hooper, *J.C.S. Dalton*, 1973, 1520.

[2] C. C. Addison, M. G. Barker, R. J. Pulham, and R. M. Lintonbon, *Chem. Soc. Special Publ.*, No. 22, 1967, 460.

[3] C. C. Addison, M. G. Barker, and R. M. Lintonbon, *J. Chem. Soc.* (*A*), 1970, 1465.

[4] C. C. Addison, M. G. Barker, and D. J. Wood, *J.C.S. Dalton*, 1972, 13.

oxide reactions with pure sodium and metal reactions with sodium containing oxygen can thus be shown to give products of a very similar nature, and this paper will discuss the significance of such in relation to the reactivity of oxygen in liquid sodium.

To investigate possible reaction mechanisms ternary oxides of sodium and niobium were exposed to pure liquid sodium, and oxygen-doped liquid sodium. The results of these experiments together with those on the reactions of the binary oxides with liquid sodium give an overall picture of the types of process occurring in this type of system.

RESULTS

Binary Oxides.—Mixtures of the transition-metal oxide with liquid sodium (in excess) were equilibrated at either 400 or 600 °C before removal of the excess of sodium by vacuum distillation at 300 °C. *X*-Ray powder diffraction patterns of the solid products remaining after distillation enabled the identification of the phases formed in the reaction to be established. The products varied in colour from dark grey to black. Results are summarised in Table 1.

TABLE 1

Reaction products of niobium and tantalum oxides with liquid sodium, at equilibrium

	Products	
Oxide	400 °C	600 °C
Nb_2O_5	$3Nb + 5Na_3NbO_4$	$3Nb + 5Na_3NbO_4$
NbO_2	$Nb + Na_3NbO_4$	$Nb + Na_3NbO_4$
NbO	No reaction	$3Nb + Na_3NbO_4$
Ta_2O_5	$3Ta + 5Na_3TaO_4$	$3Ta + 5Na_3TaO_4$

The following points may be made as regards these results: (1) In accordance with the Phase Rule two solid phases were found as equilibrium products. The ternary oxides Na_3NbO_4 and Na_3TaO_4 were always present as the face-centred cubic crystallographic modifications [5,6] in the equilibrium reactions. (2) In reactions that had not reached equilibrium the orthorhombic forms [6] of Na_3TaO_4 and Na_3NbO_4 were observed in the products; the monoclinic forms [5,6] were never observed in any reaction. (3) The relative intensities of diffraction lines due to the transition metals and the ternary oxides varied as the amounts of each product expected for particular oxide–liquid sodium reactions. (4) The *X*-ray diffraction patterns of the products of the reactions at 400 °C were diffuse; showing considerable line-broadening. The lines due to products obtained at 600 °C were sharp and well defined.

Ternary Oxides.—Reactions with pure liquid sodium. Sodium metaniobate, sodium metatantalate, the cubic form of sodium orthotantalate, and a mixture of cubic and monoclinic forms of sodium orthoniobate were equilibrated in pure liquid sodium for 2 days at 600 °C before excess of sodium was distilled off at 300 °C. The products, identified by their *X*-ray powder diffraction patterns, are given in Table 2.

The metaniobate was completely converted into the cubic orthoniobate and niobium metal at equilibrium. However, according to the Phase Rule, the products indicated for the metatantalate reaction are not at equilibrium. It appears that the metatantalate undergoes a very much slower reaction than the metaniobate, being only partially converted into the cubic orthotantalate and tantalum metal within the time allowed for the experiment. The cubic orthotantalate and the mixture of cubic and monoclinic orthoniobate remain unchanged.

TABLE 2

Reactions of ternary oxides with pure liquid sodium

Ternary oxide	Products
$NaNbO_3$	Na_3NbO_4 (f.c.c.) + Nb
$NaTaO_3$	$NaTaO_3 + Na_3TaO_4$ (f.c.c.) + Ta
Na_3TaO_4(f.c.c.)	No reaction
Na_3NbO_4 (f.c.c. + monocl.)	No reaction

The following conclusions arise from these experiments: (1) The NbO_4^{3-} and TaO_4^{3-} species are the stable species in liquid sodium at 600 °C. (2) The stability of the cubic orthoniobate relative to metaniobate is greater than that of the cubic orthotantalate relative to the metatantalate. (3) The monoclinic form of Na_3NbO_4 (and therefore probably Na_3TaO_4) is stable towards pure liquid sodium. However, the monoclinic forms of Na_3NbO_4 and Na_3TaO_4 are not observed as products in the reaction of niobium and tantalum oxides with liquid sodium, or in the corrosion of niobium or tantalum in liquid sodium.[4] It appears therefore that these compounds cannot take any part in the mechanisms of these reactions. The co-existence of the cubic and monoclinic forms of Na_3NbO_4 or Na_3TaO_4 has been observed frequently in solid-state preparations.[5,6] It is not clear which phase modification is the more thermodynamically stable under any given conditions; interconversion of the two forms must be very slow.

Reactions with oxygenated liquid sodium. Samples of $NaTaO_3$ and the cubic form of Na_3TaO_4 were heated at 600 °C in liquid sodium saturated with respect to sodium monoxide. Excess of sodium was subsequently distilled off at 300 °C. The products were similar in both cases, being mixtures of orthorhombic Na_3TaO_4, cubic Na_3TaO_4, and excess of sodium oxide. The proportion of orthorhombic form to cubic form increased with increasing reaction time.

Two important points arise from these reactions: (1) Sodium metatantalate is not stable in sodium containing oxygen at 600 °C. (2) The postulate [4] that orthorhombic Na_3TaO_4 is the alkali-rich form of the orthotantalate appears to be confirmed since excess of sodium oxide in sodium at 600 °C reacts with $NaTaO_3$ and cubic Na_3TaO_4 to produce orthorhombic Na_3TaO_4.

DISCUSSION

The relevant free energies of formation of the binary oxides of niobium,[7] tantalum,[7] and sodium oxide,[8] at 600 and 400 °C are given in Table 3. These values indicate that liquid sodium should not reduce niobium pentoxide, tantalum pentoxide, niobium dioxide, or

TABLE 3

$-\Delta G_f^\circ$ Values for niobium and tantalum oxides and sodium oxide

	$-\Delta G_f^\circ$/kcal (g-atom O)$^{-1}$				
Oxide	Nb_2O_5	NbO_2	NbO	Ta_2O_5	Na_2O
At 600 °C	74·1	75·3	79·4	79·9	69·9
At 400 °C	78·2	79·3	83·7	84·1	76·9

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[5] Y. Bouilland, *Bull. Soc. chim. France*, 1965, 519.

[6] M. G. Barker and D. J. Wood, *J.C.S. Dalton*, 1972, 9.

[7] A. Glassner, U.S.A.E.C. Report ANL-5750, 1957.

[8] C. E. Wicks and F. E. Block, U.S. Bureau of Mines, Bulletin 603, 1963.

niobium monoxide, to give niobium, or tantalum, and sodium oxide at either 600 or 400 °C, as shown by the values in Table 4. The only reaction which appears likely to occur is the reduction of niobium pentoxide to the dioxide. Further reduction to the monoxide is unfavourable at 600 °C, although favourable at 400 °C, as shown in Table 5. Tyzack[9] has suggested, on the basis of thermodynamic calculations, that Nb_2O_5 will be stable to sodium containing 100 p.p.m. oxygen, NbO_2 to sodium containing 30—40 p.p.m. oxygen, and NbO to sodium containing 5 p.p.m. oxygen. The formation of compounds such as Na_3NbO_4 and Na_3TaO_4 does, of course, invalidate such methods for the prediction of reaction products since no thermodynamic datum is yet available for these compounds.

TABLE 4

Reaction	$\Delta G°$/kcal At 600 °C	 At 400 °C
$Nb_2O_5 + 10Na \longrightarrow 2Nb + 5Na_2O$	+21	+6·5
$NbO_2 + 4Na \longrightarrow Nb + 2Na_2O$	+10·8	+4·8
$NbO + 2Na \longrightarrow Nb + Na_2O$	+5·4	+2·4
$Ta_2O_5 + 10Na \longrightarrow 2Ta + 5Na_2O$	+50	+36

TABLE 5

Reaction	ΔG/kcal At 600 °C	 At 400 °C
$Nb_2O_5 + 2Na \longrightarrow 2NbO_2 + Na_2O$	−0·6	−3·1
$NbO_2 + 2Na \longrightarrow NbO + Na_2O$	+1·4	−2

The formation of the ternary oxides must involve energy changes which are significant in comparison with the $\Delta G_f°$ values for the simple oxides. Although the $\Delta G_f°$ values for these ternary oxides are not known, the data for the binary oxides of the transition metals and sodium oxide can be used to show the approximate size of these values. For the reactions (1)—(4) to be

$$4Nb_2O_5 + 15Na \longrightarrow 3Nb + 5Na_3NbO_4 \quad (1)$$

$$2NbO_2 + 3Na \longrightarrow Nb + Na_3NbO_4 \quad (2)$$

$$4NbO + 3Na \longrightarrow 3Nb + Na_3NbO_4 \quad (3)$$

$$4Ta_2O_5 + 15Na \longrightarrow 3Ta + 5Na_3TaO_4 \quad (4)$$

thermodynamically favoured at 600 °C, the $-\Delta G_f°$ (600 °C) values for the ternary oxides must be greater than 317·6 kcal mol^{-1} for Na_3NbO_4, and 319·6 kcal mol^{-1} for Na_3TaO_4. At 400 °C reaction (3) does not take place and this gives further information, so that $-\Delta G_f°$ (400 °C) for Na_3NbO_4 must be between 317·2 and 334·8 kcal mol^{-1}.

The solid-state preparation of the cubic orthotantalate from sodium oxide and tantalum pentoxide[6] does certainly indicate that its heat of formation is very large. It is interesting to note that a number of compounds of the general formula $Na_n^{n+}AO_4^{n-}$, with $n > 1$ have large heats of formation (and therefore large free energies of formation) as illustrated in Table 6.[10] It can be pointed out that many of the compounds in Table 6 are tetrahedral in structure and therefore basically dissimilar to octahedral Na_3NbO_4 and Na_3TaO_4. However, solid-state reactions used in the formation of such tetrahedrally co-ordinated compounds as Na_3VO_4[11] and Na_4TiO_4[12] have indicated heats of formation similar to those of Na_3NbO_4 and Na_3TaO_4, and Na_4TiO_4 is stable in liquid sodium.[12]

TABLE 6

Heats of formation at 298 K of some ternary oxides (from ref. 10)

Compound	$-\Delta H_f°$/kcal mol^{-1}	Compound	$-\Delta H_f°$/kcal mol^{-1}
Na_2SO_4 $(-\Delta G_f° = 304)$	331	Na_3PO_4	460
Na_2CrO_4	318	Na_3AsO_4	365
Na_2WO_4	395	Na_3VO_4	420
Na_2UO_4	501	Na_4SnO_4	456

On the basis of free-energy values, the reaction of the niobium and tantalum oxides with liquid sodium must proceed by a mechanism other than that involving sodium oxide formation. This can be postulated as the direct atomic rearrangement of the oxide lattices into two lattices (metal and MO_4^{3-}) which together are more energetically favourable in a liquid sodium environment. The process can be more easily understood if the structures of the oxides are considered. The oxides of niobium and tantalum consist of MO_6 octahedra distorted by edge sharing, corner sharing, and/or vacancies in the structures,[13,14] whilst MO_4^{3-} compounds (M = Nb or Ta) have regular MO_6 octahedra sharing corners. The compounds Na_3MO_4 represent the maximum amount of sodium oxide that can exist with regular MO_6 octahedra and show complete corner sharing of the octahedra in the cubic phases of the ternary oxides.[6]

The conversion of binary oxides into ternary oxides must therefore involve the loss of metal atoms from the lattice and migration of oxygen atoms within the lattice such that the penetration of sodium brings about the formation of the highly stable cubic Na_3MO_4 compounds. This process may involve an MO_3^- intermediate phase since $NaMO_3$ compounds, which have structures related to those of perovskite, are converted into Na_3MO_4 compounds in liquid sodium. The process scheme may well be (5). However, $NaMO_3$ compounds have never been observed in products of reactions in liquid sodium, or during the corrosion of niobium or tantalum in liquid sodium.[4] In experiments described earlier in this paper orthorhombic Na_3TaO_4 was formed when $NaTaO_3$, and the cubic form of Na_3TaO_4, were equilibrated with liquid sodium saturated with oxygen. The complete absence of the orthorhombic forms of the compounds Na_3NbO_4 and Na_3TaO_4 from the reactions of the niobium and tantalum oxides with liquid sodium support the postulate that no sodium oxide is generated in the reaction mechanism.

$$MO_x \longrightarrow MO_3^- \longrightarrow MO_4^{3-} \text{ with } x = 1, 2, \text{ or } 2{\cdot}5 \quad (5)$$

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[9] C. Tyzack, Proc. Symp. N.W. Branch Chem. Eng., Manchester, 1964, 151.

[10] F. D. Rossini, U.S. National Bureau of Standards, Circular No. 500, 1952.

[11] M. G. Barker and A. J. Hooper, *J.C.S. Dalton*, 1973, 1513.

[12] M. G. Barker and D. J. Wood, *J.C.S. Dalton*, 1972, 2448.

[13] A. F. Wells, 'Structural Inorganic Chemistry,' Oxford University Press, London, 1962.

[14] A. Reisman, *J. Phys. Chem.*, 1962, **66**, 15.

EXPERIMENTAL

The purities of the pentoxides used in this study were Nb_2O_5, 99·99%; Ta_2O_5, 99·9%. The lower oxides of niobium, and sodium oxide, were prepared as described previously.[3,6] All reagents were stored under dry argon.

The liquid sodium was obtained directly from a circulating loop[2] and the process of allowing oxides to react with liquid sodium has been described.[2] However, in the present work excess of sodium was distilled off under vacuum at 300 °C, rather than the 450 °C used in earlier work. The use of 300 °C eliminates the possibility of any solid-state reaction occurring during distillation, since this is below the reaction temperatures of sodium oxide and the metal oxides.[6]

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