Reactions of Liquid Sodium with Transition-metal Oxides. Part VI.[1] Oxides of Vanadium

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Vanadium pentoxide is reduced by liquid sodium to the oxide V_2O_3 and sodium oxide at low temperatures (150 °C). On increasing the temperature (up to 600 °C) the ternary oxides Na_4VO_4 and $NaVO_2$ are produced. Vanadium dioxide reacts at 150 °C to form the oxide $NaVO_2$ which is stable to liquid sodium up to 600 °C. Vanadium(III) oxide, V_2O_3, reacts with liquid sodium to give a mixture of the ternary oxide, $NaVO_2$, and the monoxide, VO; the latter oxide is stable to pure liquid sodium up to 600 °C but may be oxidised by solutions of oxygen in liquid sodium to $NaVO_2$ which may be further oxidised by oxygen in sodium to Na_4VO_4.

CONSIDERATION of the free energies of formation of the vanadium oxides and sodium oxide (Table 1) shows that the reaction $10Na + V_2O_5 \longrightarrow 2V + 5Na_2O$, is favourable ($\Delta G = -81{\cdot}5$ kcal mol^{-1} V_2O_5 at 400 °C). If, however, reaction is considered to take place in a step-wise manner, then reaction will proceed only as far as the oxide V_2O_3 since further reduction to the oxide VO is unfavourable ($\Delta G = 5{\cdot}7$ kcal mol^{-1} V_2O_3 at 400 °C).

TABLE 1

Free energies of formation ($-\Delta G$ kcal per g atom O) of sodium oxide and the vanadium oxides

Temp./°C	100	200	300	400	600
Na_2O	86·7	83·1	79·1	76·9	69·9
V_2O_5	66·4	64·3	62·0	60·6	56·5
V_2O_4	77·1	75·1	72·7	71·5	67·5
V_2O_3	90·4	88·3	86·0	84·6	80·6
VO	91·2	89·2	86·9	85·6	81·6

The extent to which the higher oxides of vanadium will be reduced will, therefore, depend entirely on the mechanism of reaction. Complete reduction to the metal will only take place if reaction does not proceed by the formation of the oxide V_2O_3. Vanadium monoxide should be stable towards liquid sodium at all temperatures; it may however be oxidised by liquid sodium containing dissolved oxygen.

TABLE 2

Reaction of vanadium pentoxide with liquid sodium

Expt. no.	Reaction * temp./°C	Equilibn. temp./°C	Distilln. temp./°C	Products
(1)	150	150		$V_2O_3 + Na_2O$
(2)	300	300		$NaVO_2 + Na_4VO_4$
(3)	450	450		$NaVO_2 + Na_4VO_4$
(4)	600	600		$NaVO_2 + Na_4VO_4$
(5)	150		350	$NaVO_2 + Na_3VO_4 + VO$
(6)	300		350	$NaVO_2 + Na_3VO_4$
(7)	400		350	$NaVO_2 + Na_3VO_4$
(8)	600		350	$NaVO_2 + Na_3VO_4$
(9)	150	400	280	$NaVO_2 + Na_4VO_4 + VO$
(10)	150	400	350	$NaVO_2 + Na_3VO_4 + VO$
(11)	150	600	280	$NaVO_2 + Na_4VO_4 + VO$
(12)	150	600	350	$NaVO_2 + Na_3VO_4 + VO$

* The temperature of the liquid sodium at which the oxide was added.

Previous studies [2,3] have shown that the formation of ternary oxides seriously complicates any arguments based purely on thermodynamical considerations. It will be shown that the oxide V_2O_3 may be reduced by liquid sodium at temperatures in the region of 300 °C according to the equation: $V_2O_3 + Na \longrightarrow VO + NaVO_2$. This reaction implies that the ternary oxide $NaVO_2$ must have a free energy of formation $>171{\cdot}1$ kcal mol^{-1}, a value of the same order as that measured [4] for the similar compound, $NaCrO_2$ (ΔG -202 kcal mol^{-1} at 300 °C).

Reactions were generally carried out by adding the oxide to an excess of the liquid metal. The reaction mixture was then equilibrated at a fixed temperature and the excess of sodium then removed by vacuum distillation. The reaction of vanadium pentoxide proved to be of much greater complexity than that of the other oxides and thus some variations of the experimental techniques has to be employed.

RESULTS AND DISCUSSION

Vanadium Pentoxide.—This reacts with liquid sodium as soon as the alkali metal becomes molten. The nature of the product formed is influenced both by the temperature at which the oxide is added to the metal and by the method used to remove the excess of sodium used in the reaction (Table 2). In order to separate these effects, three experimental methods were employed.

(*a*) The oxide was added to an excess of liquid sodium at temperatures between 150 and 600 °C, equilibrated at

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[1] Part V, C. C. Addison and R. J. Pulham, *J.C.S. Dalton*, 1972, 1020.

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

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

[4] S. A. Jansson and E. Berky, 'Corrosion by Liquid Metals,' eds. J. E. Draley and J. R. Weeks, Plenum Press, New York, 1970, p. 496.

the same temperature, cooled, and the product examined (by powder *X*-ray diffraction) both as an extruded rod of sodium containing the product, and as a residue after removal of most of the sodium by filtration under argon pressure [experiments (1)—(4)] or by washing with liquid ammonia [experiment (1)].

(*b*) The oxide was added to liquid sodium at temperatures between 150 and 600 °C, the reaction mixture allowed to cool, and the excess of sodium removed by vacuum distillation at 350 °C and 10^{-5} mmHg [experiments (5)—(8)].

(*c*) The oxide was added to liquid sodium at 150 °C, the reaction mixture equilibrated at either 400 or 600 °C, and the excess of sodium removed by vacuum distillation at either 350 or 280 °C [experiments (9)—(12)].

Identification of Reaction Products.—The oxides V_2O_3, VO, and Na_2O were identified by comparison of their *X*-ray powder diffraction patterns with those reported in ref. 5, and Na_3VO_4 and $NaVO_2$ by comparison of their patterns with those already established[6] by us previously. The compound Na_4VO_4, which had not been previously reported, was prepared in a pure state by the reaction of excess of liquid sodium with the sodium vanadate Na_3VO_4; the excess of sodium was removed by vacuum distillation at 280 °C (Found: Na, 45·0; V, 24·2. Na_4VO_4 requires Na, 44·45; V, 24·6%). Magnetic measurements, by the room-temperature Gouy method, gave μ_{eff} 2·23 B.M. The *X*-ray powder diffraction pattern is given in Table 3.

TABLE 3

X-Ray powder diffraction pattern of the compound

d/Å	*h k l*	*I*/*I*₀	*d*/Å	*h k l*	*I*/*I*₀
5·34	2 1 0	18	2·544	1 5 1	8
5·04	1 2 1	85	2·391	0 4 3	100
4·57	1 0 2	50	2·349	3 2 3	85
4·36	2 2 0	30	2·245	5 0 1	95
4·36	2 2 0	30	2·198	3 3 3	5
4·11	0 3 1	15	2·122	2 6 0	25
3·90	1 3 1	55	2·006	5 3 1	4
3·612	2 1 2	45	1·811	5 2 3	4
3·327	0 3 2	18	1·684	5 0 4	4
3·193	1 0 3	30	1·664	1 6 4	18
2·765	4 0 1	55	1·646	1 0 6	8
2·691	0 3 3	80	1·629	2 8 0	18
2·665	2 2 3	95	1·601	1 2 6	25

The assignment of Miller indices is based on an orthorhombic unit cell with $a = 11{\cdot}520$, $b = 13{\cdot}587$, and $c = 9{\cdot}978$ Å.

The compound was found to be relatively unstable, decomposing under vacuum at 290 °C, with the loss of sodium to give the orthovanadate Na_3VO_4: $Na_4VO_4 \longrightarrow Na_3VO_4 + Na$.

Mechanism of Reaction.—The results of experiment (1) (Table 2) indicate that between 100 and 150 °C the oxide V_2O_5 is reduced to V_2O_3 and sodium oxide. At temperatures between 300 and 600 °C [experiments (2)—(4)] V_2O_3 is not produced but reaction proceeds directly to the compounds $NaVO_2$ and Na_4VO_4. If V_2O_5 is added to liquid sodium at 150 °C and the temperature then raised [experiments (5) and (9)—(12)] the V_2O_3 produced at 150 °C reacts further at the higher temperature to give $NaVO_2$ and VO: $V_2O_5 + 5Na \longrightarrow NaVO_2 + VO + 2Na_2O$. Both these compounds are stable to pure sodium, but separate experiments have shown that both may be oxidised by liquid sodium containing dissolved sodium oxide. The compound $NaVO_2$ is oxidised to Na_4VO_4, and vanadium monoxide is oxidised initially to $NaVO_2$ and, if sufficient sodium oxide is available, to Na_4VO_4 also. Thus these two reactions may be regarded as competing for the available sodium oxide produced in the initial reaction at the melting point of the sodium. Neither the monoxide VO nor the compound $NaVO_2$ are totally oxidised in the reactions studied: thus both appear as components of the reaction products, together with Na_4VO_4.

Further justification for this mechanism was obtained from the reaction of the oxide V_2O_3 with liquid sodium to which had been added 2 mol of sodium oxide per mol of V_2O_3; the products of reaction were identical with those from experiments (5), (10), and (12) where the experimental conditions were analogous.

The presence of the orthovanadate Na_3VO_4 as a reaction product in several of the experiments is merely a consequence of the distillation temperature. This compound is unstable towards liquid sodium but is formed by loss of sodium on distillation at 350 °C from Na_4VO_4.

Vanadium Dioxide.—Liquid sodium reacts with vanadium dioxide at 155 °C to give the ternary oxide, $NaVO_2$, which is stable to liquid sodium up to 600 °C (the maximum temperature studied) and is unaffected *in vacuo* at temperatures up to 660 °C. All experimental evidence suggests that the compound is formed by direct reaction, there being no initial reduction to the oxide V_2O_3 and sodium oxide.

The formation of vanadium sesquioxide would have led, under the experimental conditions employed, to the production of the monoxide, VO, as a reaction product. The *X*-ray diffraction patterns, chemical analyses (Table 4), and magnetic measurements all gave good evidence for only a single phase, $NaVO_2$, being formed.

Further evidence was obtained from the reacting of $V_2O_3 : V_2O_5$ 1 : 1 with sodium which gave Na_4VO_4, $NaVO_2$, and VO; reduction of V_2O_5 took place first to give $V_2O_3 : Na_2O$ 1 : 1. The mechanism of reaction of vanadium dioxide with sodium is therefore characteristic of the oxide, rather than of the V : O stoicheiometry of 1 : 2.

The *X*-ray diffraction patterns of the compounds $NaVO_2$ were always diffuse and it was not possible to detect the line-splittings observed from the products of solid-state preparations. The *X*-ray pattern, was, however, sufficiently definite to enable an unambiguous assignment to be made.

Vanadium Sesquioxide and Vanadium Monoxide.—Differential thermal analysis (d.t.a.) showed that the reaction between liquid sodium and the oxide V_2O_3 is not greatly exothermic at temperatures <400 °C. No

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[5] A.S.T.M. Powder Diffraction Data File, Joint Committee for Powder Diffraction Standards, Philadelphia.

[6] M. G. Barker and A. J. Hooper, preceding papers.

reaction was observable by the d.t.a. method, but *X*-ray diffraction patterns of the product showed that reaction had taken place <300 °C. The product gave a diffuse pattern which could be interpreted as being a mixture of two phases, the oxide VO, and the compound $NaVO_2$: $V_2O_3 + Na \longrightarrow NaVO_2 + VO$. Products which had been heated in liquid sodium at 600 °C showed much better crystallinity and identification was conclusive.

The reaction of the oxide V_2O_3 with liquid sodium is analogous to that of niobium pentoxide with liquid potassium. The formation of the ternary oxide, $NaVO_2$, enables reduction to proceed to a lower oxidation state than is otherwise possible.

TABLE 4

Chemical analyses

Oxide	Equilibn. temp./°C	Distilln. temp./°C	Found/% Na	Found/% V	Found/% O	Calc./% Na	Calc./% V	Calc./% O	Stoicheiometry
(*a*) Excess of Na									
V_2O_5	450	*a*	31·3	38·6	30·3	31·7	38·9	30·5	$NaVO_2 + Na_4VO_4$
VO_2	400	350	21·5	48·2	30·3	21·7	48·1	30·2	$NaVO_2$
VO_2	600	350	21·5	48·3	30·2	21·7	48·1	30·2	$NaVO_2$
V_2O_3	300	280	13·3	59·0	27·7	13·3	58·9	27·8	$NaVO_2 + VO$
V_2O_3	600	280	13·4	58·3	28·3	13·3	58·9	27·8	$NaVO_2 + VO$
Na_3VO_4	400	280	45·0	24·2	30·8	44·4	24·6	30·9	Na_4VO_4
Na_3VO_4	400	350	37·7	27·7	34·6	37·5	27·7	34·8	Na_3VO_4
(*b*) Stoicheiometric Na									
V_2O_3	400		13·3	58·7	28·0	13·3	58·9	27·8	$NaVO_2 + VO$
VO_2	400		21·9	47·9	30·2	21·7	48·1	30·2	$NaVO_2$

[a] NH_3 Extraction.

Vanadium monoxide does not react with liquid sodium either at 400 or 600 °C. The oxide extracted from liquid sodium was unchanged when the alkali metal contained only 10 p.p.m. of oxygen. The addition of the non-stoicheiometric monoxide ($VO_{0.85}$) to liquid sodium containing a small quantity of sodium oxide led to the formation of $NaVO_2$ together with the monoxide, with an unchanged lattice constant. With increasing quantities of sodium oxide, complete oxidation to $NaVO_2$ takes place. With large additions of sodium oxide $NaVO_2$ is subsequently oxidised to the compound Na_4VO_4.

Stoicheiometric Reactions.—Experiments carried out with an excess of liquid sodium indicated that the following reactions occur:

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\begin{gathered}
2V_2O_5 + 7Na \longrightarrow 3NaVO_2 + Na_4VO_4 \\
VO_2 + Na \longrightarrow NaVO_2 \\
V_2O_3 + Na \longrightarrow NaVO_2 + VO
\end{gathered}
$$

In order to verify these reactions, experiments were carried out in which the oxides were added to the stoicheiometric quantities of sodium represented in the equations. In all instances reaction gave a product which was a fine powder and *X*-ray diffraction patterns showed only the presence of the predicted compound; no sodium or unreacted vanadium oxide was detected. The compound $NaVO_2$ thus formed was crystalline and the low-temperature line-splitting effect was clearly observed. The use of stoicheiometries other than those represented in these equations always led to the presence of unreacted starting products.

Chemical Analyses.—Generally samples only partially dissolved in water and where necessary complete solution was effected by addition of 20 vol. hydrogen peroxide. Vanadium was estimated by titration of V^{4+} in solution (obtained by sulphur dioxide reduction) with potassium permanganate. Sodium was determined by flame photometry. Results are shown in Table 4.

EXPERIMENTAL

Reagents.—Sodium containing 5—10 p.p.m. oxygen was taken from a laboratory sodium loop. AnalaR vanadium pentoxide was dried to constant weight. Vanadium dioxide was prepared by the solid-state reaction of the pentoxide with the sesquioxide V_2O_3 at 650 °C under argon, which was itself obtained by hydrogen reduction of V_2O_5 at 650 °C. Vanadium monoxide, both stoicheiometric and non-stiocheiometric, was prepared by the solid-state reaction of vanadium metal and the pentoxide at 1200 °C under vacuum.

Sodium oxide was prepared as described in ref. 7. The techniques used in reactions involving an excess of sodium have been described previously.

For reactions involving a stoicheiometric quantity of sodium, the molten metal was measured out by volume, by use of a pre-calibrated capillary pipette. The sodium was heated to the required temperature and the correct weight of transition-metal oxide was then added in a single addition.

The d.t.a. apparatus is described in ref. 6.

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