Reactions of Sodium Oxide with the Oxides VO_2, V_2O_3, VO, and Vanadium Metal

By **Marten G. Barker** * and **Alan J. Hooper**, Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD

The reactions of sodium oxide with vanadium metal and its lower oxides are described for different molar ratios of reactants. All reaction products are identified by powder X-ray crystallography and the reaction temperature determined by differential thermal analysis.

No ternary oxides containing vanadium in the 4+ state were formed in the reactions of sodium oxide with vanadium dioxide; an equimolar mixture gave $NaVO_2$ and Na_3VO_4. The ternary oxide $NaVO_2$ was prepared by the reaction of vanadium(III) oxide with sodium oxide in equimolar proportions, but sodium orthovanadate Na_3VO_4 was formed at higher sodium oxide concentrations. This product was also formed from reactions of the monoxide and vanadium metal with sodium oxide.

THE sodium oxide–vanadium pentoxide system has been studied to some extent,[1-4] but little is known about the reactivity of sodium oxide with the lower oxides of vanadium. Reactions of this type are of interest not only because of the possibility of forming new ternary oxides containing vanadium in an oxidation state lower than +5, but also as a pointer towards the reactivity of vanadium metal with sodium oxide in solution in liquid sodium.

Three ternary oxides of vanadium have so far been reported[5] with vanadium in an oxidation state lower than +5: Na_2VO_3, prepared by the reaction of sodium azide with sodium metavanadate at 320 °C in vacuum, $Na_2V_2O_5$ by the reaction of vanadium pentoxide and sodium azide, and $NaVO_2$ by the reaction[6] of vanadium dioxide and sodium azide at 500 °C. Chemical analyses of the last two compounds showed that only 72 and 97% of the vanadium was in the expected 4+ oxidation state.

We describe here the reactions of sodium oxide with the oxides VO_2, V_2O_3, and VO for different molar ratios of reactants. All reaction products have been identified by powder X-ray diffraction methods and in certain reactions differential thermal analysis has been used to determine the reaction temperature.

RESULTS AND DISCUSSION

Reactions of Sodium Oxide with Vanadium Dioxide.—The reaction products and their conditions of preparation are summarised in Table 1. No ternary oxides containing vanadium in the +4 oxidation state were found as products of these reactions.

The product of experiment (1) consisted of a mixture of $NaVO_2$ and Na_3VO_4. Pouchard[7] reported that the products of a 1 : 1 mixture of sodium oxide and vanadium dioxide heated at 500 °C in a sealed silica capsule gave an X-ray pattern in good agreement with that given by Rudorff.[8] The compound was poorly crystalline and was not isostructural with the corresponding compounds Na_2TiO_3, Na_2SnO_3, and Na_2ZrO_3. The X-ray pattern given by Pouchard may also be interpreted on the basis of a mixture containing the compounds $NaVO_2$ and Na_3VO_4, the latter being present entirely in the cubic modification.[3] Table 2 shows the X-ray powder pattern given by the 1 : 1 reaction product together with the reported patterns of Na_2VO_3 and those of $NaVO_2$ and Na_3VO_4.

TABLE 1

Products and reaction conditions for sodium oxide–vanadium dioxide. All reactions were at 550 °C for 24 h under argon

Expt. No.	$Na_2O : VO_2$	Products
(1)	1 : 1	Na_3VO_4 (IV), $NaVO_2$
(2)	1 : 2	α-$Na_4V_2O_7$, β-$Na_4V_2O_7$, V_2O_3
(3)	2 : 1	Na_3VO_4 (III), Na_3VO_4 (IV), Na
(4)	1 : 3	$Na_2V_3O_7$ ($Na_{1\cdot8}V_2O_5$)
(5)	1 : 5	$Na_2V_5O_{11}$ ($Na_{1\cdot3}V_2O_5$)

There is excellent correlation of d values, but that of the relative intensities of diffraction lines is less good, particularly for the lines of $NaVO_2$. This is almost certainly due to the low crystallinity of the reaction product of experiment (1).

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[2] A. A. Fotiev and B. V. Slobodin, *Zhur. priklad. Khim.*, 1965, **38**, 801.

[3] M. G. Barker and A. J. Hooper, preceding paper.

[4] G. Le Flem and R. Olazcuaga, *Bull. Soc. chim. France*, 1968, 2769.

[5] W. Rüdorff and H. Becker, *Z. Naturforsch.*, 1954, **9b**, 613.

[6] W. Rüdorff and H. Becker, *Z. Naturforsch.*, 1954, **9b**, 614.

[7] M. Pouchard, Ph.D. Thesis, University of Bordeaux, 1967.

[8] W. Rüdorff, G. Walter, and H. Becker, *Z. anorg. Chem.*, 1956, **285**, 287.

The differential thermal analysis (d.t.a.) trace given by this product shows that two transitions take place between room temperature and 600 °C. An endothermic transition at 75°, which was found to be reversible, may readily be assigned to the well known phase change of the dioxide VO_2. A large exothermic peak represented the reaction of sodium oxide with vanadium dioxide at 265 °C. An approximate heat of reaction may be calculated from the ratio of the peak areas by use of the known[9] heat of phase transition (ΔH 750 cal mol^{-1} VO_2) of vanadium dioxide. The value determined by this method was ΔH (265 °C) = —33·2 kcal mol^{-1} VO_2.

TABLE 2

X-Ray diffraction data given by the product from the reaction of $Na_2O : VO_2$ (1 : 1)

Product		Na_2VO_3 [a]		Na_2VO_3 [b]		$NaVO_2$		Na_3VO_4 (IV) [c]	
d/Å	I/I_0	d/Å	I/I_0 [d]	d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
5·60	5	5·50	w	5·62	8	5·62	55		
5·35	25			5·37	15	5·37	55		
4·42	80	4·41	m	4·40	90			4·40	90
				4·17	5				
				3·914	5				
3·80	30	3·80	w	3·814	25			3·80	45
2·801	3					2·818	10		
2·706	100	2·70	s	2·696	100	2·691	22	2·702	100
2·571	5			2·561	5	2·574	10		
2·461	15			2·466	12	2·475	25		
						2·383	4		
2·290	5			2·305	8			2·304	15
2·186	70	2·18	s	2·179	40	2·186	100	2·199	6
2·149	1					2·159	15		
						2·118	10		
						2·099	3		
						2·080	1		
1·912	20	1·916	m	1·909	20			1·914	25
1·748	1					1·743	4	1·757	8
1·721	2					1·728	10		
1·698	2					1·707	1	1·705	2
1·593	15			1·591	10	1·595	25		
1·557	20	1·574	w	1·560	15			1·564	18
1·498	10	1·505	m			1·501	12		
		1·239	m						

[a] Ref. 8. [b] Ref. 7. [c] Ref. 3. [d] w = Weak, m = medium, s = strong.

The powder *X*-ray diffraction pattern of the product of a reaction carried out in the d.t.a. apparatus, with a maximum temperature just above the reaction temperature, was identical to that obtained from a reaction in which heating had been continued to 600 °C. There is, therefore, no experimental evidence to suggest that the compound Na_2VO_3 is formed in the reaction of sodium oxide and vanadium dioxide.

The compound $Na_2V_2O_5$ could not be prepared by the reaction of 1 mol of sodium oxide and 2 mol of vanadium dioxide [experiment (2)]. A previous attempt to prepare $Na_2V_2O_5$ by the reaction of an equimolar mixture of sodium pyrovanadate $Na_4V_2O_7$ and vanadium(III) oxide V_2O_3, at 500 °C in a sealed silica ampoule proved fruitless as the reactants were found to be unchanged. Using a similar type of reaction Pouchard[10] was however able to prepare three non-stoicheiometric compounds with structures closely related to vanadium bronzes of the type $Na_xV_2O_5$. The direct reaction of sodium oxide and vanadium oxide [Table 1, experiments (4) and (5)] in the molar ratios 1 : 3 and 1 : 5 gave products identical to those reported by Pouchard for the same sodium to vanadium ratios.

The reaction of vanadium dioxide with 2 mol of sodium oxide [Table 1 experiment (3)] did not give the compound Na_4VO_4. The loss of sodium was observed during reaction, and the final product gave an *X*-ray powder diffraction corresponding to the orthovanadate Na_3VO_4: $VO_2 + 2Na_2O \longrightarrow Na_3VO_4 + Na$.

In the sodium oxide-rich region no compounds may be prepared by the solid-state reaction of sodium oxide with vanadium dioxide, which contain vanadium in the 4+ oxidation state. Disproportionation was observed with the formation of either the 5+ state or mixtures of the 5+ and 3+ states. This type of behaviour is fairly typical of the 4+ oxidation state of vanadium, similar disproportionation reactions being found for some of the binary halides.

Reactions of Sodium Oxide with Vanadium(III) *Oxide*.—The reactivity of sodium oxide with the oxide V_2O_3 is considerably lower than with the other vanadium oxides. In order to achieve complete reaction experiments were carried out at 810 °C in sealed silica ampoules under argon [experiments (1)—(4), Table 2].

TABLE 2

Reactions of sodium oxide with vanadium(III) oxide

Expt. no.	Reactants	Products
(1)	$Na_2O + V_2O_3$	$NaVO_2$
(2)	$Na_2O + V_2O_3$	$NaVO_2$
(3)	$2Na_2O + V_2O_3$	$\frac{3}{2}NaVO_2 + \frac{1}{2}Na_3VO_4$ (IV) + Na
(4)	$3Na_2O + V_2O_3$	$NaVO_2 + Na_3VO_4$ (IV) + 2Na
(5)	$Na_2O + NaVO_2$	$NaVO_2$, Na_3VO_4 (IV), Na_3VO_4 (III), Na
(6)	$2Na_2O + NaVO_2$	Na_3VO_4 (IV), Na_3VO_4 (III), Na

The reactants in experiments (1) and (4) were used in the form of compressed pellets and were in contact with the silica ampoule. The powder *X*-ray diffraction patterns of the products from these two reactions showed the presence of an extra phase which is probably formed by the interaction of the reactants with silica. The powder *X*-ray diffraction patterns of the products from the remaining experiments (in which the sample was enclosed in platinum foil) did not show the presence of lines due to this impurity.

The compound $NaVO_2$ gave a powder *X*-ray diffraction pattern, which closely resembled that of the hexagonal phase, α-$NaFeO_2$. Line-splitting effects were, however, observed from all the preparations. The lines corresponding to reflections from the 003, 006, 104, 107, and 113 Miller planes in a hexagonal structure were clearly resolved into doublets. The effect was most pronounced for the reflection from the 003 plane, which gave two strong diffraction lines with the interplanar spacings d 5·62 and 5·37 Å. On heating the sample

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[9] T. Kawakubo and T. Nakagawa, *J. Phys. Soc. Japan*, 1964, **19**, 517.

[10] M. Pouchard, A. Casalot, L. Rabardel, and P. Hagenmuller, *Bull. Soc. chim. France*, 1968, 2742.

in a high temperature X-ray diffractometer attachment, the distorted form transformed, at *ca.* 200 °C, to regular hexagonal phase, giving a diffraction pattern exactly analogous to that of the compound α-$NaFeO_2$. On cooling to room temperature the distorted form was obtained. The X-ray diffraction patterns of the two forms of the compound $NaVO_2$ are given in Table 3.

TABLE 3

X-Ray diffraction patterns of $NaVO_2$ modifications

$NaVO_2$ (25 °C)		$NaVO_2$ (200 °C)				
d/Å	I/I_0	d/Å	h	k	l	I/I_0
5·62	55	5·44	0	0	3	55
5·37	55					
2·818	10	2·714	0	0	6	15
2·691	22					
2·574	10	2·564	1	0	1	12
2·475	25	2·468	1	0	2	22
2·405	5					
2·383	4					
2·186	100	2·183	1	0	4	100
2·159	15					
2·118	10					
2·099	3					
2·080	1	2·025	1	0	5	2
1·743	4	1·734	1	0	7	12
1·728	10					
1·707	1					
1·595	25	1·603	1	0	8	20
1·501	12	1·498	1	1	0	15
1·446	5	1·445	1	1	3	5
1·435	5					
1·408	3					
1·372	4	1·378	1	0	10	5

a 3·00 Å, *c* 16·30 Å

An increase in the sodium oxide content [experiments (3) and (4), Table 2] gave Na_3VO_4 as a reaction product. Sodium metal was evolved, and the silica capsule was therefore severely attacked by the alkali metal. The compound Na_3VO_4 may be obtained as the sole product from the reaction at 550 °C of sodium oxide (2 mol) with $NaVO_2$ (1 mol) either in vacuum or argon [experiment (6)]. It is, therefore, this reaction, taking place after the formation of $NaVO_2$, which gives rise to the formation of the orthovanadate in experiments (3)—(5) (Table 2). Pure $NaVO_2$ may readily be prepared by the hydrogen reduction of the metavanadate, $NaVO_3$, at 600 °C. The distorted form is obtained from this reaction.

Reaction of Sodium Oxide with Vanadium Monoxide and Vanadium Metal.—The reactants, in the form of intimately mixed powders, were heated under vacuum to 575 °C, and the reaction products (Table 4) identified by X-ray powder diffraction.

TABLE 4

Reactions of sodium oxide with vanadium monoxide and vanadium metal

Expt. No.	Reactants	Products
(1)	$Na_2O + 2VO$	$VO + NaVO_2 + Na_3VO_4$ (IV) + Na
(2)	$Na_2O + VO$	$VO + NaVO_2 + Na_3VO_4$ (IV) + Na
(3)	$3Na_2O + 2VO$	$VO + NaVO_2 + Na_3VO_4$ (IV) + Na_3VO_4 (III) + Na
(4)	$2Na_2O + VO$	$VO + NaVO_2 + Na_3VO_4$ (IV) + Na_3VO_4 (III) + Na
(5)	$5Na_2O + 2VO$	$VO + Na_3VO_4$ (IV) + Na_3VO_4 (III) + Na
(6)	$3Na_2O + VO$	Na_3VO_4 (IV) + Na_3VO_4 (III) + Na
(7)	$Na_2O + V$	β-V + $NaVO_2 + Na_3VO_4$ (IV) + Na_3VO_4 (III) + Na
(8)	$2Na_2O + V$	β-V + Na_3VO_4 (IV) + Na_3VO_4 (III) + Na
(9)	$3Na_2O + V$	β-V + Na_3VO_4 (IV) + Na_3VO_4 (III) + Na
(10)	$4Na_2O + V$	Na_3VO_4 (IV) + Na_3VO_4 (III) + Na

The quantity of Na_3VO_4 increased from experiments (1)—(5) at the expense of the compound $NaVO_2$ and the monoxide VO. These observations, together with the presence of unreacted vanadium monoxide, suggest the following reaction mechanism. First, sodium oxide reacts with vanadium monoxide to give the compound $NaVO_2$ [equation (1)].

$$Na_2O + VO \longrightarrow NaVO_2 + Na \qquad (1)$$

The compound $NaVO_2$ is however unstable towards sodium oxide being oxidised to the orthovanadate Na_3VO_4 [equation (2)]. Reaction (2) is

$$2Na_2O + NaVO_2 \longrightarrow Na_3VO_4 + 2Na \qquad (2)$$

obviously favoured over reaction (1), but only in experiment (6) is the sodium oxide–vanadium monoxide ratio great enough for complete reaction [equation (3)].

$$3Na_2O + VO \longrightarrow Na_3VO_4 + 3Na \qquad (3)$$

The presence[11] of β-V in the products of experiments (7)—(9) suggests that, initially, sodium oxide reacts with vanadium metal in such a way that oxygen enters the metal lattice with the formation of a solid solution [equation (4)]. The behaviour of vanadium containing

$$V + Na_2O \longrightarrow V(O) + Na \qquad (4)$$

dissolved oxygen may then be regarded as being analagous to that of the monoxide.

The presence of two forms of Na_3VO_4 in the reaction products is a consequence of the reaction conditions. The compound Na_3VO_4 (III) will be slowly transformed to the compound Na_3VO_4 (IV) at these temperatures under vacuum and hence both forms are observed in the reaction products.

EXPERIMENTAL

Reagents.—Sodium oxide was prepared as described previously.[12] Vanadium dioxide was prepared by the solid-state reaction of the pentoxide V_2O_5 with the sesquioxide V_2O_3 at 650 °C under argon. Vanadium sesquioxide was prepared by the hydrogen reduction of V_2O_5 at 650°, and the monoxide, VO, by the solid-state reaction of vanadium metal and the pentoxide at 1200 °C under vacuum.

The methods used for the solid-state reactions of sodium oxide with transition metal oxides is described in ref. 12. The d.t.a. apparatus used was described in ref. 3.

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