Reactions of the Oxides of Vanadium with Liquid Potassium

By **Marten G. Barker,* Alan J. Hooper,** and **Roger M. Lintonbon,** Department of Chemistry, The University, Nottingham NG7 2RD

The reactions of the oxides V_2O_5, V_2O_3, VO_2, and VO with liquid potassium have been studied at temperatures up to 400 °C. The oxides V_2O_5 and VO_2 react at 63 °C (the m.p. of potassium); V_2O_3 at 180 °C; and VO was found not to react at up to 400 °C. The new compound KVO_2 was identified as the only reaction product of the dioxide VO_2 with liquid potassium. The pentoxide V_2O_5 and the oxide V_2O_3 gave the oxides VO and KVO_2 as reaction products, but both these compounds were found to oxidise to the ternary oxide K_3VO_4 in the presence of dissolved oxygen in the liquid metal. The behaviour of liquid potassium towards the oxides of vanadium is compared with the other alkali metals, lithium and sodium.

We are investigating the mechanism and products of reactions between the liquid alkali metals and oxides of the transition metals.[1] Previous papers dealt with vanadium oxides and liquid lithium [2] and liquid sodium,[3] and we now report on reactions of liquid potassium.[4]

The free energies of formation, at 400 °C, of the oxides in this system are in Table 1. These data indicate that the only oxide which could be reduced directly to vanadium metal, with the formation of potassium monoxide, is vanadium pentoxide. However, even with this oxide reduction to a lower oxide is thermodynamically more favourable [reactions (1)—(3)]. Thus,

TABLE 1

Free energies of formation of oxides at 400 °C [a]

Oxide	$-G_f^0$ (400 °C) kcal mol^{-1}	$-G_f^0$ (400 °C) kcal (g-atom O)$^{-1}$
V_2O_5	303·2	60·6
VO_2	143·0	71·5
V_2O_3	253·6	84·5
VO	85·5	85·5
K_2O	62·4	62·4

1 cal = 4·184 J throughout this paper.
[a] Ref. 5.

$$V_2O_5 + 10K \longrightarrow 2V + 5K_2O; \quad \Delta G^0 \text{ (400 °C)} = -8{\cdot}8 \text{ kcal (mol } V_2O_5)^{-1} \qquad (1)$$

$$V_2O_5 + 4K \longrightarrow V_2O_3 + 2K_2O; \quad \Delta G^0 \text{ (400 °C)} = -75{\cdot}2 \text{ kcal (mol } V_2O_5)^{-1} \qquad (2)$$

$$V_2O_5 + 6K \longrightarrow 2VO + 3K_2O; \quad \Delta G^0 \text{ (400 °C)} = -53{\cdot}0 \text{ kcal (mol } V_2O_5)^{-1} \qquad (3)$$

the lower oxides of vanadium are likely products in these systems.

The reactions of the vanadium oxides with liquid potassium were investigated by heating reaction mixtures at various temperatures for seven days under reduced pressure in sealed Pyrex capsules. The method[3] of examining reaction products by extruding a rod of the alkali metal for powder *X*-ray analysis was not easily applied to this system. The products were not dispersed throughout the alkali metal but tended to settle at the base of the reaction tube, where it was not possible to remove samples for extrusion. Therefore the reaction products were generally isolated by vacuum distillation at 250 °C, this being the minimum temperature for reasonable rate of distillation.

Reaction of Vanadium Pentoxide with Liquid Potassium.—Reactions were carried out at 100, 200, 300, and 400 °C. Powder *X*-ray analysis of the black products, isolated by vacuum distillation at 260 °C, showed the presence of the same compounds in all products. For each reaction the products were as in (4). The quantity of K_3VO_4

$$K + V_2O_5 \longrightarrow VO + KVO_2 + K_3VO_4 \qquad (4)$$

(as the cubic modification) in the reaction product increased with the temperature of reaction. Since attack on the Pyrex vessel by the potassium increased with temperature, it seemed likely that the formation of the compound K_3VO_4 could be associated with the increasing potassium monoxide content of the potassium from reaction (5) with the silica in the Pyrex tube.

$$K + SiO_2 \longrightarrow 2K_2O + Si \qquad (5)$$

Mechanism of Reaction.—The similarity of the reaction products to those obtained by the reaction of the pentoxide with liquid sodium[3] suggests that an identical reaction mechanism may be postulated. Reduction may take place in a stepwise manner (6) to the oxide

$$V_2O_5 + 4K \longrightarrow V_2O_3 + 2K_2O \qquad (6)$$

V_2O_3. This oxide then reacts (7) to give KVO_2 and the

$$V_2O_3 + K \longrightarrow KVO_2 + VO \qquad (7)$$

oxide VO. At this point the overall reaction can be represented as (8). Both KVO_2 and VO can be oxidised

$$V_2O_5 + 5K \longrightarrow KVO_2 + VO + 2K_2O \qquad (8)$$

in liquid potassium by the monoxide K_2O, in each case the product being the ternary oxide K_3VO_4. In the

---

[1] C. C. Addison, M. G. Barker, and A. J. Hooper, *J.C.S. Dalton*, 1972, 1017.
[2] C. C. Addison, M. G. Barker, and J. Bentham, *J.C.S. Dalton*, 1972, 1035.
[3] M. G. Barker and A. J. Hooper, *J.C.S. Dalton*, 1973, 1520.
[4] C. C. Addison, M. G. Barker, and R. M. Lintonbon, *J. Chem. Soc.* (*A*), 1970, 1465.
[5] F. D. Rossini, ' Selected Values of Chemical Thermodynamic Properties,' U.S. Nat. Bur. Standards Circ. 500, 1952.

liquid-sodium reactions the product of the last step was the ternary oxide Na_4VO_4. Only after vacuum distillation did the compound Na_3VO_4 appear as a reaction product [reaction (9)]. Since vacuum distillation was

$$Na_4VO_4 \longrightarrow Na_3VO_4 + Na \qquad (9)$$

used in this work to remove the excess of potassium from the reaction products it was essential that the stability of K_3VO_4 to liquid potassium be verified and the reaction product be examined in the presence of potassium metal.

A sample of the compound K_3VO_4 was heated in excess of potassium at 400 °C. *Ca.* 90% of the excess of potassium was removed by vacuum distillation and the extrusion technique was applied to the remainder of the metal which now contained sufficient reaction product for identification by *X*-ray powder diffraction. The product consisted largely of unchanged K_3VO_4(IV) together with a small quantity of the more oxygenated phase K_3VO_4(III). Thus in liquid potassium the compound K_3VO_4 is not reduced to K_4VO_4 but may be slightly oxidised by the small traces of dissolved monoxide always present in the potassium.

Chemical Analysis.—The equations derived from the reaction mechanism give an overall stoicheiometry for the reaction product of $K_3V_2O_5$ (Found for the product of reaction at 100 °C: K, 39·9; V, 33·5. Calc. for $K_3V_2O_5$: K, 39·2; V, 34·1%). The slight discrepancy can be satisfactorily accounted for by the quantity of potassium monoxide present in the potassium. For a corresponding reaction, with liquid potassium with a slightly higher oxygen content, a stoicheiometry of $K_{3\cdot3}V_2O_{5\cdot2}$ was obtained.

Reaction of Vanadium Dioxide with Liquid Potassium.—Reactions were carried out at 100, 200, 300, and 400 °C. Powder *X*-ray analysis of the black reaction products, isolated by vacuum distillation at 260 °C, showed them, in each case, to consist largely of the compound KVO_2 together with a small quantity of K_3VO_4. Again the quantity of K_3VO_4 increased with the temperature of reaction.

Characterisation of the Compound KVO_2.—*Chemical analysis.* Analysis of the product of the reaction carried out at 100 °C (Found: K, 35·5; V, 41·4. Calc. for KVO_2: K, 32·0; V, 41·7%) showed this sample of KVO_2 to contain only a very small quantity of K_3VO_4(IV) impurity.

Magnetic measurements. At 29·2 °C $\mu_{eff} = 1{\cdot}63$ B.M., close to values published for other alkali metal–vanadium(III) oxides. Such a consideration does not however take account of the different structures, and consequent intermolecular magnetic interactions, exhibited by these compounds.

Decomposition in vacuo. A slight evolution of vapour was observed above 300 °C. The pressure generated above the compound greatly increased at *ca.* 550 °C and observable quantities of potassium were evolved. Powder *X*-ray analysis of the sample after this heat treatment showed the presence of V_2O_3 and the compound K_3VO_4(IV). It therefore appears that a somewhat unusual decomposition (10) occurs *in vacuo.* The

$$5KVO_2 \longrightarrow K_3VO_4 + 2V_2O_3 + 2K \qquad (10)$$

weight loss was in good agreement with this formulation. Decomposition (10) is a further indication of the low stability of KVO_2 and can be explained by assuming an initial decomposition (11) to the oxides V_2O_3 and K_2O

$$2KVO_2 \longrightarrow V_2O_3 + K_2O \qquad (11)$$

followed by the interaction (12). The compound

$$5K_2O + V_2O_3 \longrightarrow 2K_3VO_4 + 4K \qquad (12)$$

$NaVO_2$ has an analogous initial decomposition (13) but

$$2NaVO_2 \longrightarrow V_2O_3 + Na_2O \qquad (13)$$

sodium monoxide reacts with the oxide V_2O_3 much less readily than potassium monoxide.

Reaction with potassium monoxide. When a 2 : 1 K_2O–KVO_2 mixture was heated to 350 °C *in vacuo*, potassium was evolved. Powder *X*-ray analysis of the product showed the presence of K_3VO_4(IV) and small quantities of K_3VO_4(III). Reaction clearly proceeds as in (14).

$$KVO_2 + 2K_2O \longrightarrow K_3VO_4 + 2K \qquad (14)$$

Reaction of Vanadium Sesquioxide with Liquid Potassium.—Reactions were carried out at 300 and 400 °C. Powder *X*-ray analysis of the black products, isolated by vacuum distillation at 260 °C, showed the presence of vanadium monoxide (VO), KVO_2, and traces of K_3VO_4(IV) with more K_3VO_4(IV) in the product from reaction carried out at 400 °C.

Reaction of Vanadium Monoxide with Liquid Potassium.—Reaction was carried out at 400 °C. Powder *X*-ray analysis of the product, isolated by vacuum distillation at 260 °C, showed only the presence of VO. On repetition of the reaction, after addition of a small quantity of potassium monoxide to the potassium, the vanadium monoxide isolated after reaction showed a considerable stoicheiometry range. The broad powder *X*-ray diffraction lines given by this product corresponded to a range of compositions upwards of $VO_{1\cdot0}$ with respect to oxygen content. Clearly small quantities of potassium monoxide dissolved in potassium interact with the oxide VO to increase its oxygen content rather than to give a reaction of the type (15)

$$K(O) + VO \longrightarrow KVO_2 \qquad (15)$$

as observed in liquid sodium.

This phenomenon has also been observed for the powder *X*-ray diffraction patterns given by VO in the products from the reactions of vanadium pentoxide and vanadium sesquioxide with liquid potassium.

Reactions of the Vanadium Oxides with the Liquid Alkali Metals.—Table 2 shows the products formed in the reactions of liquid lithium, sodium, and potassium with the vanadium oxides. The behaviour of liquid lithium is clearly different from that of both sodium and potassium since the high free energy of formation [5] of lithium oxide [$-\Delta G_f°(298\ K) = 133{\cdot}8$ kcal mol^{-1}] enables the direct reduction of the oxides to the metal and lithium oxide. No interaction between lithium oxide and the vanadium metal was observed in these reactions. The formation of binary and ternary nitrides was achieved, however, by the addition of the less stable nitride Li_3N to the system. The behaviour of liquid potassium closely resembles that of liquid sodium, with only small differences in the type of compounds formed. (i) The compound K_3VO_4 is stable to liquid potassium whereas the sodium orthovanadate, Na_3VO_4, interacts with liquid sodium to give the compound Na_4VO_4. (ii) Vanadium monoxide is not reduced by either liquid sodium or liquid potassium, but is oxidised by the alkali-metal monoxide to the compound $NaVO_2$ in liquid sodium and to a more oxygenated stoicheiometry in liquid potassium.

TABLE 2

Reactions of liquid lithium,[2] sodium,[3] and potassium with the vanadium oxides

Oxide	Product in lithium	Product in sodium	Product in potassium
V_2O_5	$V + Li_2O$	$Na_4VO_4 + NaVO_2 + VO$	$K_3VO_4 + KVO_2 + VO$
VO_2	$V + Li_2O$	$NaVO_2$	KVO_2
V_2O_3	$V + Li_2O$	$NaVO_2 + VO$	$KVO_2 + VO$
VO	$V + Li_2O$	No reaction	No reaction

EXPERIMENTAL

The Lower Oxides of Vanadium.—Vanadium dioxide was prepared by the solid-state reaction of vanadium pentoxide and vanadium sesquioxide at 650 °C, vanadium sesquioxide by hydrogen reduction of vanadium pentoxide at 650 °C, and vanadium monoxide by the solid-state reduction of vanadium sesquioxide with vanadium metal at 1200 °C under vacuum.

Liquid Potassium.—The purification of liquid potassium, and its reaction with transition-metal oxides, have been described.[4]

[3/1085 *Received, 25th May*, 1973