# Reactions of Potassium Monoxide with the Oxides of Vanadium

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The alkali-rich portion of the $K_2O$–$V_2O_5$ system has been investigated by the reaction of various potassium oxo-compounds with vanadium pentoxide. The compounds $KVO_3$, $K_{32}V_{18}O_{61}$, $K_4V_2O_7$, and $K_3VO_4$ lose oxygen and three forms of the compound $K_3VO_4$ were established. Both oxidations and disproportionations were observed for the $K_2O$–$VO_2$ system, and a new compound $KVO_2$ was found in the reaction of equimolar mixtures of the monoxide $K_2O$ and vanadium dioxide. The lower oxides of vanadium and vanadium metal were oxidised by potassium monoxide to the vanadate $K_3VO_4$. The reactions of potassium monoxide are compared with those of sodium oxide for the same stoicheiometry.

ALKALI-RICH ternary oxides containing potassium and vanadium in the +5 oxidation state have been well characterised by Holtzberg and his co-workers.[1] However, in the light of work on the sodium oxide–vanadium pentoxide system [2] the potassium oxide–vanadium pentoxide system was re-investigated.

No ternary oxide containing potassium and vanadium in a more reduced oxidation state than +5 has been reported. Consequently the reactions of potassium oxide with lower oxides of vanadium and vanadium metal are of interest and have been carefully examined.

Solid-state work on these systems was complicated by two difficulties. First, the powder *X*-ray diffraction patterns given by reaction products were poor, showing very few diffraction lines of appreciable intensity. Further, the products of interest all had their most intense diffraction lines in the same narrow range of *d*-values, between 3·15 and 2·80 Å. Secondly, potassium monoxide undergoes thermal decomposition [3] at 446 °C and is very sensitive to oxygen.

*The Potassium Oxide–Vanadium Pentoxide System.*—The compounds $KVO_3$, $K_{32}V_{18}O_{61}$, and $K_4V_2O_7$ were prepared by heating mixtures of potassium carbonate and vanadium pentoxide, in corresponding 1 : 1, 16 : 9, and 2 : 1 molar ratios, to 700 °C in a stream of oxygen. The reactions were followed by thermogravimetric analysis (Table 1) which showed in each case a weight loss of the reaction mixture corresponding to complete evolution of carbon dioxide. The compounds all gave *X*-ray diffraction patterns in good agreement with those of Holtzberg *et al.*, although slight differences between the two sets of data for $KVO_3$ occurred in the intensities of some diffraction lines. All our products from t.g.a. were coloured, whereas the compounds prepared by Holtzberg *et al.* were white.[4] Although the preparations were carried out in an oxygen stream it appears that oxygen had been lost with the creation of some reduced centres. This was confirmed by the fact that $KVO_3$ and $K_4V_2O_7$ showed weak paramagnetism in excess of that predicted purely on the basis of paramagnetism due to

TABLE 1

Thermogravimetric analysis of $K_2CO_3$–$V_2O_5$ reaction mixtures

| | | Product | | Wt. loss (%) | |
|---|---|---|---|---|---|
| $K_2CO_3 : V_2O_5$ | $t$/°C | Colour | $\mu_{eff}$/B.M. at 24 °C | Obs. | Calc. |
| 1 : 1 | 700 | Pale orange | 0·53 | 13·74 | 13·75 |
| 16 : 9 | 700 | Very pale green | — | 18·27 | 18·29 |
| 2 : 1 | 700 | Grey-green | 0·78 | 19·19 | 19·20 |
| 3 : 1 | 800 | Bright blue | 1·15 | 23·04 | 22·13 |

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[1] F. Holtzberg, A. Reisman, M. Berry, and M. Berkenblit, *J. Amer. Chem. Soc.*, 1956, **78**, 1536.

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

[3] P. Touzain, F. Brisse, and M. Caillet, *Canad. J. Chem.*, 1970, **48**, 3358.

[4] M. Pouchard, Thesis, University of Bordeaux, 1967.

combined vanadium pentoxide in the compounds.[5] Oxygen stirring, as recommended by Holtzberg and his co-workers, therefore seems necessary in order to prepare samples without loss of oxygen.

Further to investigate the loss of oxygen, we performed two other preparations of the metavanadate $KVO_3$. Reaction of KOH with $V_2O_5$ in 2 : 1 molar ratio at 500 °C gave a product showing only slight colour with a powder *X*-ray diffraction pattern in excellent agreement with that of Holtzberg *et al.* A low-temperature preparation of the metavanadate by the reaction of KOH with $NH_4VO_3$ in aqueous solution gave a product which on drying at 140 °C and subsequent grinding was yellow-white. Magnetic measurements gave $\mu_{eff} = 0{\cdot}497$ B.M. at 25·1 °C and the *X*-ray pattern was in perfect agreement with that published by Holtzberg *et al.*

The sample prepared at low temperature was also examined by high-temperature *X*-ray diffractometry but no structural change was observed up to the m.p. (518 °C). This contrasts with the behaviour of sodium metavanadate which changes structure at 405 °C. During repeated temperature cycling, changes in the relative intensities of some diffraction lines were observed. These may be attributed to loss of oxygen during heating under the helium used.

The use of potassium hydroxide in solid-state preparations at 500 °C of $K_{32}V_{18}O_{61}$ and $K_4V_2O_7$ gave whiter samples than those obtained from solid-state preparations from carbonate.

*Potassium Orthovanadate*, $K_3VO_4$.—T.g.a. of a 3 : 1 $K_2CO_3$–$V_2O_5$ mixture (Table 1) showed kinetic behaviour very similar to that for the reaction of a 3 : 1 $Na_2CO_3$–$V_2O_5$ mixture. Potassium pyrovanadate $K_4V_2O_7$ was formed fairly rapidly, but its reaction with a further mole of potassium carbonate to give potassium orthovanadate required almost 4 h at 800 °C. The weight loss of the reaction mixture after this heating period was in excess (by 0·91 total weight %) of that calculated for evolution of 3 mol of carbon dioxide [reaction (1)].

$$3K_2CO_3 + V_2O_5 \longrightarrow 2K_3VO_4 + 3CO_2 \qquad (1)$$

The product was bright blue which indicated that the additional weight loss could be assigned to substantial loss of oxygen. Further evidence of oxygen loss was the value of $\mu_{eff} = 1{\cdot}15$ B.M. at 23·3 °C.

An identical preparation under air rather than oxygen gave very similar results. This product had $\mu_{eff} = 1{\cdot}17$ B.M. at 23·2 °C showing partial reduction of the vanadium +5 centres to have occurred to a similar extent in both preparations. The powder *X*-ray diffraction patterns given by these products were identical. All but one of the diffractions observed could be assigned to a ZnS-type cubic structure, with $a = 8{\cdot}30$ Å. All the diffraction lines of this ZnS-type cubic phase occurred with the same relative intensities in the diffraction pattern reported by Holtzberg and his co-workers for $K_3VO_4$. The diffraction pattern reported by those workers contained several lines additional to those corresponding to the ZnS-type cubic phase. Of these the most intense (at $d = 2{\cdot}83$ Å) corresponded to the one outstanding diffraction line in the diffraction pattern of the products obtained from t.g.a. preparations. Undoubtedly the preparation of $K_3VO_4$ by Holtzberg *et al.* gave a two-phase product, one of these phases being a ZnS-type cubic phase.

It appears that the behaviour of the potassium oxide–vanadium pentoxide system, at a composition of 75 mol % alkali-metal monoxide, is exactly analogous to the behaviour of the sodium oxide–vanadium pentoxide system at this composition.[2] The use of oxygen stirring by Holtzberg and his co-workers inhibited oxygen loss from 3 : 1 $K_2CO_3$–$V_2O_5$ mixtures more than the presence of an oxygen atmosphere. Consequently the preparations in the t.g.a. apparatus gave a product containing predominantly the phase associated with high oxygen loss, whereas Holtzberg *et al.* obtained a considerable quantity of a more oxygenated phase-modification.

A pure sample of the cubic phase was obtained by heating a sample of $K_3VO_4$, prepared under oxygen, in a stream of argon at 800 °C for 2 h. This phase will be referred to as $K_3VO_4$(IV) by analogy with the cubic phase of $Na_3VO_4$.[2] The more oxygenated form of the potassium orthovanadate will therefore be referred to as $K_3VO_4$(III), this being the phase having the most intense line of its diffraction pattern at $d = 2{\cdot}83$ Å. The complete *X*-ray diffraction patterns of these phases are given in Table 2.

TABLE 2

*X*-Ray diffraction pattern of $K_3VO_4$(IV)

| $d$/Å | *hkl* | $I/I_0$ | $d$/Å | *hkl* | $I/I_0$ |
|---|---|---|---|---|---|
| 4·79 | 111 | 18 | 2·076 | 400 | 12 |
| 4·15 | 200 | 8 | 1·695 | 422 | 10 |
| 2·931 | 220 | 100 | 1·595 | 333 | 4 |
| 2·512 | 311 | 2 | 1·469 | 440 | 4 |
| 2·399 | 222 | 10 | 1·402 | 531 | 2 |

*X*-Ray diffraction pattern of $K_3VO_4$(III)
(From Holtzberg *et al.*, for $K_3VO_4$)

| $d$/Å | $I/I_0$ | $d$/Å | $I/I_0$ |
|---|---|---|---|
| 5·29 | vw | 2·83 | s |
| 4·54 | w | 2·24 | w |
| 3·76 | vvw | 1·88 | vvw |
| 3·56 | vw | 1·83 | vw |
| 3·22 | w | 1·72 | vw |
| 3·12 | m | | |

The use of potassium hydroxide instead of the carbonate gave, from reaction at 600 °C, a product which was still predominantly $K_3VO_4$(IV), but contained rather more of the oxygenated phase $K_3VO_4$(III).

The reaction of potassium monoxide with both the pentoxide (in 3 : 1 molar ratio) and the metavanadate (in 1 : 1 molar ratio) at 350 °C for 24 h under argon gave products which were composed of both $K_3VO_4$(IV) and

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[5] Handbook of Chemistry and Physics, 45th edn., The Chemical Rubber Co., Cleveland, Ohio, 1964—65, E62.

$K_3VO_4$(III). In both cases the mixture had clearly fused during an extremely exothermic reaction.

A sample of $K_3VO_4$(IV) heated at 600 °C *in vacuo* for 24 h decomposed with the loss of potassium monoxide to the pyrovanadate, $K_4V_2O_7$. Although decomposition was not complete, $K_3VO_4$ is clearly much less thermally stable than sodium orthovanadate, $Na_3VO_4$, which does not begin to decompose below 800 °C under vacuum. This difference can be attributed to the higher volatility of potassium monoxide.

*Reactions of Potassium Monoxide with Vanadium Dioxide*.—This reaction was investigated for molar ratios between 1 : 3 and 2 : 1 (Table 3). Except for experiment 5, the reactants were heated as intimately mixed powders.

TABLE 3

Reactions of potassium monoxide with vanadium dioxide

| No. | Reactants | Atmosphere | $t$/°C | Time/h | Products |
|---|---|---|---|---|---|
| 1 | $K_2O + 3VO_2$ | Argon | 350 | 24 | $K_2V_3O_7$ |
| 2 | $K_2O + 2VO_2$ | Argon | 350 | 24 | $K_4V_2O_7$, $V_2O_3$ |
| 3 | $K_2O + VO_2$ | Argon | 350 | 24 | $K_4V_2O_7$, $KVO_2$, K |
| 4 | $K_2O + VO_2$ | Argon | 425 | 24 | $K_4V_2O_7$, $K_3VO_4$(IV), $V_2O_3$, K |
| 5 | $2K_2O + VO_2$ | Argon | 300 | 2 | $K_3VO_4$(I), K |
| 6 | $K_3VO_4$(I) | Vacuum | 260 | 24 | $K_3VO_4$(IV), $K_3VO_4$(III) |

The powder *X*-ray diffraction pattern of $K_2V_3O_7$ (experiment 1) was in excellent agreement with the powder *X*-ray data quoted by Pouchard[4] for the stoicheiometric hypovanadate $K_2V_3O_7$ prepared by reaction (2). Reaction (3) of a 1 : 2 mixture of $K_2O$ and

$$4KVO_3 + K_4V_2O_7 + 3V_2O_3 \longrightarrow 4K_2V_3O_7 \quad (2)$$

$$2K_2O + 4VO_2 \longrightarrow K_4V_2O_7 + V_2O_3 \quad (3)$$

$VO_2$ proceeds analogously to reaction (4) in the same molar ratio. The disproportionation of $V^{4+}$ into the

$$2Na_2O + 4VO_2 \longrightarrow Na_4V_2O_7 + V_2O_3 \quad (4)$$

$V^{5+}$ and $V^{3+}$ states was also observed for reaction (5) in

$$3K_2O + 3VO_2 \longrightarrow K_4V_2O_7 + KVO_2 + K \quad (5)$$

1 : 1 molar ratio, but reaction (5) shows certain differences from the analogous reaction (6) in 1 : 1 molar ratio.

$$2Na_2O + 2VO_2 \longrightarrow Na_3VO_4 + NaVO_2 \quad (6)$$

First, potassium was evolved in the reaction at 240 °C and secondly the compound $K_4V_2O_7$ was produced in preference to the orthovanadate, $K_3VO_4$. The reasons for these differences are not yet understood. The compound $KVO_2$ has not been reported previously. The larger ionic radius of the $K^+$ ion dictates a change in structure for this compound from the hexagonal–rhombohedral structure, observed for $AMO_2$-type compounds where A = Li or Na, to the $KFeO_2$-type cubic structure.[6] The powder *X*-ray diffraction pattern of $KVO_2$ closely resembles that of the ZnS-type cubic phase-modification of potassium orthovanadate in respect of line positions. On the basis of systematic absences and relative intensities of diffraction lines, the pattern could be indexed satisfactorily as being isostructural with $KFeO_2$, with a cell dimension $a = 8{\cdot}41$ Å (Table 4). This indexing was later substantiated when an almost pure sample of $KVO_2$ was obtained.[7]

TABLE 4

*X*-Ray diffraction patterns

| $KFeO_2$ | | | $KVO_2$ | | |
|---|---|---|---|---|---|
| $d$/Å | $hkl$ | $I/I_0$ | $d$/Å | $hkl$ | $I/I_0$ |
| 4·61 | 111 | 40 | 4·89 | 111 | 35 |
| 2·83 | 220 | 100 | 2·969 | 220 | 100 |
| 2·31 | 222 | 10 | 2·522 | 222 | 10 |
| 2·00 | 400 | 40 | 2·132 | 400 | 30 |
| 1·83 | 331 | 10 | 1·944 | 331 | 10 |
| 1·63 | 422 | 80 | 1·734 | 422 | 50 |
| 1·54 | 511<br>333 | 10 | 1·633 | 511<br>333 | 5 |
| 1·41 | 440 | 30 | 1·488 | 440 | 20 |

Heating a 1 : 1 mixture of potassium monoxide and vanadium dioxide at a higher temperature (experiment 4) gave different products, the overall reaction being (7).

$$6K_2O + 6VO_2 \longrightarrow K_4V_2O_7 + 2K_3VO_4 + V_2O_3 + 2K \quad (7)$$

Absence of $KVO_2$ indicates that this phase had effectively decomposed (8). The potassium monoxide generated

$$2KVO_2 \longrightarrow K_2O + V_2O_3 \quad (8)$$

then reacts (9) with the pyrovanadate $K_4V_2O_7$ to form potassium orthovanadate. This seems to indicate that

$$K_4V_2O_7 + K_2O \longrightarrow 2K_3VO_4 \quad (9)$$

$KVO_2$ has very low thermal stability.

It was thought that the product of experiment 5 would be the compound $K_4VO_4$, and in order to prevent any loss of potassium and the formation of potassium orthovanadate $K_3VO_4$ the reactants were heated in the form of a compressed pellet. However, potassium was evolved at 240 °C, and the product was almost white. Its powder *X*-ray diffraction pattern showed no resemblance to those of $K_4TiO_4$, $K_4SnO_4$, or $K_4PbO_4$, which compose an isostructural series[8] to which it seemed likely that $K_4VO_4$ would belong since $Na_4VO_4$ is isostructural with $Na_4TiO_4$ and $Na_4PbO_4$. Therefore, it was assumed that the compound $K_4VO_4$ had not been prepared.

Much gas was evolved when the reaction product was heated at 260 °C *in vacuo* (experiment 6), the products after 24 h being $K_3VO_4$(III) and $K_3VO_4$(IV). It seems likely, therefore, that reaction (10) of potassium mon-

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[6] J. Barth, *J. Chem. Phys.*, 1935, **3**, 324.

[7] M. G. Barker, A. J. Hooper, and R. M. Lintonbon, following paper.

[8] M. Tournoux and M. Devalette, *Bull. Soc. chim. France*, 1965, 2337.

oxide with vanadium dioxide, in 2 : 1 molar ratio, yields a highly oxygenated form of the compound $K_3VO_4$.

$$2K_2O + VO_2 \longrightarrow K_3VO_4 + K \qquad (10)$$

By analogy with the sodium oxide–vanadium pentoxide system, this phase will be referred to as $K_3VO_4$(I). Its *X*-ray diffraction pattern is in Table 5.

*Reactions of Potassium Monoxide with Vanadium Sesquioxide, Vanadium Monoxide, and Vanadium Metal.*—Mixtures of potassium monoxide and vanadium sesquioxide, with stoicheiometric ratios varying from 1 : 1 to 5 : 1, were heated in the form of intimately mixed powders to temperatures in the range 260—600 °C both under dry argon and *in vacuo*. Unchanged vanadium sesquioxide was detected in the products of all reactions with less than 5 mol of potassium monoxide per mol of vanadium oxide. Only reaction (11) gave a single

$$5K_2O + V_2O_3 \longrightarrow 2K_3VO_4 + 4K \qquad (11)$$

product. Reaction was much more rapid *in vacuo* than in argon, complete reaction taking place within a few minutes at 260 °C. The product of such a reaction *in vacuo* consisted almost entirely of the highly oxygenated phase-modification of potassium orthovanadate $K_3VO_4$(I), provided that heating was stopped as soon as the evolution of potassium ceased. Longer heating periods gave further oxygen loss with the formation of the phase-modification $K_3VO_4$(IV).

Table 5

*X*-Ray diffraction pattern of $K_3VO_4$(I)

| $d$/Å | $I/I_0$ | $d$/Å | $I/I_0$ | $d$/Å | $I/I_0$ | $d$/Å | $I/I_0$ |
|---|---|---|---|---|---|---|---|
| 5·16 | 20 | 2·79 | 50 | 2·23 | 40 | 1·87 | 20 |
| 4·29 | 40 | 2·71 | 40 | 2·18 | 20 | 1·82 | 20 |
| 3·54 | 20 | 2·62 | 30 | 2·12 | 30 | 1·78 | 20 |
| 3·12 | 80 | 2·58 | 100 | 2·07 | 30 | 1·72 | 20 |
| 2·94 | 50 | 2·44 | 30 | 1·98 | 40 | 1·63 | 20 |
| 2·88 | 50 | 2·38 | 10 | 1·94 | 40 | 1·60 | 20 |

Potassium monoxide reacts with vanadium monoxide and vanadium metal in a similar manner to sodium monoxide. In the reactions investigated, the reactants were heated as intimately mixed powders at 350 °C for 24 h *in vacuo*. The products were found to be as in (12)—(15). The highly oxygenated phase-modification

$$K_2O + 2VO \longrightarrow K_3VO_4(IV) + KVO_2 + K + VO \qquad (12)$$

$$3K_2O + VO \longrightarrow K_3VO_4(IV) + K \qquad (13)$$

$$K_2O + V \longrightarrow K_3VO_4(IV) + \beta\text{-}V_xO + K + \alpha\text{-}V \qquad (14)$$

$$4K_2O + V \longrightarrow K_3VO_4(IV) + K \qquad (15)$$

of potassium orthovanadate, $K_3VO_4$(I), could be obtained from reaction of a **4 : 1** mixture of potassium monoxide and vanadium metal by heating the reactants only until potassium ceased to be evolved.

## EXPERIMENTAL

Potassium monoxide was prepared by the reaction of potassium nitrate with excess of liquid potassium at 170 °C. After reaction the excess of potassium was removed by vacuum distillation at 260 °C. This was more satisfactory than the earlier method [9,10] which involved the partial oxidation of liquid potassium. The earlier method gives potassium superoxide on the surface of the metal which is later reduced to the monoxide on distillation of the excess of potassium. We have found that the addition of the solid potassium nitrate to liquid potassium is controllable and less likely to cause ignition than the argon–oxygen or nitrogen–oxygen mixtures used in the partial oxidation method. The product, a white powder, was extremely photosensitive, turning brown after a few days in sunlight. The high reactivity of the compound necessitated the use of an oxygen- and water-free cover gas during all experiments.

Vanadium dioxide was prepared by the solid-state reaction of vanadium pentoxide and vanadium sesquioxide at 650 °C under argon, vanadium sesquioxide by hydrogen reduction of the pentoxide at 650 °C, and vanadium monoxide by the solid-state reaction of the sesquioxide and vanadium powder at 1200 °C under vacuum.

*Solid-state Reactions.*—Mixtures involving potassium oxide were made up either as intimately mixed powders or as compressed pellets in an argon-filled dry-box. The mixtures were placed in nickel containers and loaded into silica tubes fitted with a vacuum-tight tap. The silica tubes were removed from the dry-box and the volume above the tap flushed with purified argon. The temperature of the reactants was slowly raised to the required level, the excess of pressure in the reaction tube being periodically released. All products were handled under dry inert atmospheres.

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[9] R. Kohlmuller, Thesis, Université de Paris, 1959.

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