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THE REACTIONS OF THE OXIDES Cu_2O AND CuO WITH POTASSIUM MONOXIDE AND LIQUID POTASSIUM

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Summary

The ternary oxides KCuO and K_4CuO_3 have been observed as products in the solid state reactions of potassium oxide with the oxides Cu_2O and CuO under argon and in vacuum. The compound K_4CuO_3 has been isolated as a single phase and its X-ray powder diffraction pattern has been obtained. Both Cu_2O and CuO are reduced by liquid potassium to copper metal, with the formation of the ternary oxides KCuO and K_4CuO_3. Thermal analysis showed that Cu_2O reacts with liquid potassium at 185 °C and that CuO undergoes the same reaction at 70 °C.

1. Introduction

Previous publications have described reactions between liquid potassium and transition metal oxides [1 - 3] in which ternary oxides are present in the reaction products, even though existing thermodynamic data [4] would predict the formation of only the metal and potassium oxide. In this paper we present the reactions of the oxides Cu_2O and CuO with liquid potassium and with potassium oxide, the latter in the solid state.

Thermodynamic data show that the reaction

$$2K + Cu_2O \longrightarrow K_2O + 2Cu$$

is favourable to the extent of 137.4 kJ mol^{-1} at 700 K and that the reaction

$$2K + CuO \longrightarrow K_2O + Cu$$

is favourable to the extent of 164.0 kJ mol^{-1} at the same temperature. Previous experience has shown that ternary oxide formation may take place between the potassium oxide, probably in solution in the liquid potassium, and the copper metal formed in the above reactions. The particular ternary oxide which will be present in these reactions will be that which is stable towards liquid potassium containing a certain level of dissolved oxygen.

Since the only ternary oxides of potassium and copper which have been well characterized are KCuO [5] and $KCuO_2$ [6], it was decided to investigate the reactions of potassium oxide with Cu_2O and CuO to determine whether other compounds could be prepared in this system.

2. Experimental

2.1. Potassium monoxide

This compound was prepared by the reaction of potassium nitrate with an excess of liquid potassium at 170 °C. After the reaction the excess of potassium was removed by vacuum distillation at 260 °C.

2.2. Purification of potassium

Commercial potassium was freed from hydrocarbon oil by refluxing under nitrogen with low boiling petroleum (b.p. 100 - 120 °C), decanting the organic layer and degassing at 250 °C under vacuum. The metal was finally purified by filtration [1] at 70 °C through a glass sinter into a round bottomed flask. Analyses of potassium purified in this way showed oxygen contents in the range 102 - 106 ppm oxygen.

2.3. Thermal analysis of nickel oxide–liquid potassium reaction mixtures

This was carried out in sealed glass capsules. Liquid potassium (5 ml) was transferred by a glass pipette from the round-bottomed flask to the glass capsule in an argon-filled evacuable dry-box. The potassium was allowed to cool to room temperature, the nickel oxide was added and the capsule was sealed under reduced argon pressure. The reactions in the range 60 - 400 °C were followed on a simple thermal analysis apparatus; sample mixing was obtained by vibrating the capsule and the furnace on a mechanical shaker. Attack on the glass capsules by liquid potassium becomes severe above 400 °C and precludes thermal analysis above this temperature.

2.4. Isolation of reaction products

The glass capsules were broken open in an argon-filled dry-box and excess potassium was removed from the products by vacuum distillation at 190 °C. X-ray powder diffraction photographs were taken with Cu K_α radiation using a Debye–Scherrer camera 114.6 mm in diameter. During exposure the samples were contained in sealed Lindemann glass capillaries.

2.5. Solid state reactions

These were carried out using intimate mixtures of reactants prepared in an argon-filled dry-box and loaded into silica tubes fitted with a vacuum-tight tap. The reaction tubes were then either evacuated or flushed with dry argon and the samples were heated to the required temperature by an electrical furnace.

TABLE 1

Solid state reactions between K_2O and Cu_2O

Expt. no.	Reactants	Products
1	$K_2O + Cu_2O$	KCuO
2	$3K_2O + 2Cu_2O$	KCuO
3	$2K_2O + Cu_2O$	$KCuO + K_4CuO_3$
4	$3K_2O + Cu_2O$	K_4CuO_3

3. Results

3.1. Reactions of potassium monoxide with cuprous oxide

A series of solid state reactions was carried out between potassium monoxide and cuprous oxide in the molar ratios (K_2O:Cu_2O) 1:1, 3:2, 2:1 and 3:1, the reactions being carried out under an argon atmosphere at 400 °C for a period of 1 h. A brown coloration on the silica reaction tube indicated the evolution of potassium from the 3:1 reaction. The reaction products, in the form of a fused mass, were handled in an argon-filled glove box and were subjected to powder X-ray analysis. The phases observed on the powder X-ray photographs are shown in Table 1.

The product of reaction 4, the compound K_4CuO_3, has not been reported previously and was characterized by chemical analysis. The copper content was determined by atomic absorption spectroscopy and the potassium content by flame photometry. Analysis showed: K, 56.6%; Cu, 24.1%. Calculated values for K_4CuO_3 are K, 58.4%; Cu, 23.7%. The powder X-ray data for the compound are presented in Table 2. The fact that only K_4CuO_3 was observed as a single phase on the powder X-ray photograph and that the result for the copper analysis was below the copper content of the reactants, indicates that some copper metal was also formed in the reaction. No copper was observed on the X-ray photograph and in the analysis because a separation of the copper and the compound K_4CuO_3 occurred during the reaction. The 3:1 reaction was repeated in a gold crucible; the bulk of the reaction products were removed and the gold crucible was washed to remove any adherent products. When the loose material had been dissolved away, a copper film was observed on the crucible.

The four solid state reactions studied may therefore be represented by the equations:

$$K_2O + Cu_2O \longrightarrow 2KCuO \quad (1)$$

$$3K_2O + 2Cu_2O \longrightarrow 4KCuO + 2K + \frac{1}{2}O_2 \quad (2)$$

$$4K_2O + 2Cu_2O \longrightarrow 3KCuO + K_4CuO_3 + K \quad (3)$$

$$3K_2O + Cu_2O \longrightarrow K_4CuO_3 + Cu + 2K + \frac{1}{2}O_2 \quad (4)$$

TABLE 2

The X-ray diffraction pattern of K_4CuO_3

d_{obs} (Å)	I/I_0	d_{obs} (Å)	I/I_0
7.23	30	2.058	10
4.48	30	1.999	5
4.30	5	1.935	5
4.09	5	1.890	30
3.95	30	1.857	10
3.63	10	1.776	20
3.33	10	1.705	10
3.03	70	1.664	20
2.964	5	1.604	20
2.898	50	1.554	20
2.797	40	1.503	20
2.633	100	1.444	20
2.542	30	1.406	10
2.512	15	1.386	10
2.404	30	1.364	5
2.347	30	1.345	20
2.254	5	1.319	5
2.151	40	1.258	5
2.089	10		

3.2. Reactions of potassium monoxide with cupric oxide

A series of solid state reactions were carried out between potassium monoxide and cupric oxide in the molar ratios (K_2O:CuO) 1:2, 1:1, 3:2, 2:1 and 3:1. The reactions were carried out under an argon atmosphere at 400 °C and in vacuum at 300 °C for a period of 1 h. The reaction products were handled in an argon-filled glove box and were subjected to powder X-ray analysis, the results of which are presented in Table 3.

The unknown phase observed in reactions 1, 6 and 7 is the same phase in each case. Only a few lines in the powder diffraction pattern may be attributed to this phase, the strongest reflections being at d values of 2.75 Å, 4.48 Å and 5.05 Å.

The formation of the compound K_4CuO_3, as a single phase, from the reaction

$$2K_2O + CuO \longrightarrow K_4CuO_3$$

is further confirmation of the formula of the compound. In addition no potassium was observed to distil out of the reaction carried out under vacuum; this is consistent with the above formulation.

Apart from the difference between experiments 2 and 7 (Table 3), the reaction products obtained from reactions under argon are identical with those obtained from reactions in vacuum. If the reactions between potassium monoxide and cuprous oxide are compared with reactions of the same stoichiometry and conditions in this system (reactions 2 - 5), the same trends are

TABLE 3

Solid state reactions between K_2O and CuO

Expt. no.	Reactants	Atmosphere	Products
1	$K_2O + 2CuO$	Argon	KCuO + unknown phase
2	$K_2O + CuO$	Argon	KCuO
3	$3K_2O + 2CuO$	Argon	$KCuO + K_4CuO_3$
4	$2K_2O + CuO$	Argon	K_4CuO_3
5	$3K_2O + CuO$	Argon	$K_4CuO_3 + K_2O$
6	$K_2O + 2CuO$	Vacuum	KCuO + unknown phase
7	$K_2O + CuO$	Vacuum	KCuO + unknown phase
8	$3K_2O + 2CuO$	Vacuum	$KCuO + K_4CuO_3$
9	$2K_2O + CuO$	Vacuum	K_4CuO_3
10	$3K_2O + CuO$	Vacuum	$K_4CuO_3 + K_2O$

apparent. The formation of the compound KCuO is observed initially. As the amount of potassium monoxide is increased, the compound K_4CuO_3 forms along with KCuO; at higher concentrations of potassium monoxide a single phase of K_4CuO_3 is observed. The difference between the reactions of cuprous and cupric oxides with potassium monoxide is that the addition of an extra mole of potassium monoxide is required to form K_4CuO_3 from Cu_2O. The extra potassium monoxide is required because copper is being oxidized from the + 1 to the + 2 oxidation state when K_4CuO_3 is obtained from Cu_2O, whereas no oxidation occurs when K_4CuO_3 is obtained from CuO.

Reactions 5 and 10 illustrate the fact that the compound K_4CuO_3 does not react with potassium monoxide under the conditions employed in those reactions.

The formation of the ternary oxide KCuO from the reaction of a 1:1 molar mixture of K_2O and Cu_2O is in agreement with the preparation described by Hesterman and Hoppe [5] who used a 1.05:1 molar ratio of reactants heated at a temperature of 600 °C in an argon atmosphere. The compound $KCuO_2$ was not observed in our reactions since this compound can only be prepared in an oxygen atmosphere [7] or by the use of potassium superoxide as a reactant [8].

3.3. The reactions of cuprous and cupric oxides with liquid potassium

Reactions were carried out between the copper oxides Cu_2O and CuO and liquid potassium, both in sealed glass capsules and in open nickel crucibles.

3.3.1. Reactions in nickel crucibles

The copper oxides Cu_2O and CuO were reacted with liquid potassium in open nickel crucibles contained in a steel distillation vessel at 400 °C for 24 h. The excess potassium was then distilled off under vacuum. Because the expected reduction products were potassium monoxide and copper, a distil-

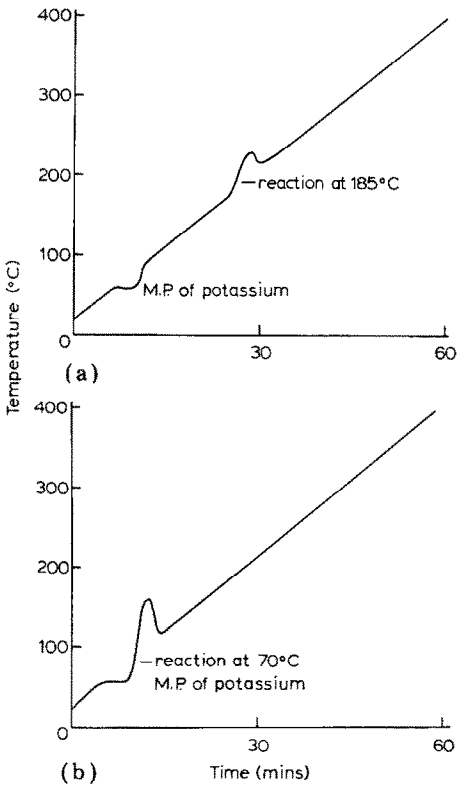

Fig. 1. Thermal analysis traces of liquid potassium–copper oxide reactions: (a) K + Cu_2O; (b) K + CuO.

lation temperature had to be employed below which these compounds did not interact. The temperature was determined by carrying out a series of solid state reactions in vacuum between potassium monoxide and copper at various temperatures. Reactions were carried out at 300 °C and 200 °C for a period of 24 h. A reaction occurred at 300 °C and the compound K_4CuO_3 was found along with unreacted starting materials. No reaction was found to occur at 200 °C, therefore the potassium was distilled off at 190 °C and 10^{-5} mmHg.

Powder X-ray analysis of the products from both reactions in liquid potassium showed them to be identical; the reaction products were metallic copper and the compound KCuO.

3.3.2. Reactions in sealed glass capsules

The copper oxides Cu_2O and CuO were reacted with liquid potassium, and a thermal analysis was carried out on each reaction. The thermal analysis traces obtained are presented in Fig. 1. Large exothermic reactions were observed in each case; Cu_2O reacted with the liquid potassium at 185 °C and CuO reacted immediately the potassium melted, at 70 °C. The melting of the potassium shows up as an endothermic peak in each case. The reactions were

equilibrated at 400 °C for 24 h; the excess potassium was then distilled off at 190 °C and 10^{-5} mmHg. The products were handled in an argon-filled glove box and were subjected to powder X-ray analysis. The powder X-ray data revealed that the products from the two reactions were identical; in both cases metallic copper and the compound K_4CuO_3 were formed.

4. Discussion

Neither the reactions in open nickel crucibles nor the reactions in sealed glass capsules gave the thermodynamically predicted products, potassium monoxide and copper metal. Both types of reaction gave copper metal and a ternary oxide; the identity of the ternary oxide depended on the type of vessel used for the reaction. Reaction in a nickel vessel produced the ternary oxide KCuO.

$$K + 2CuO \longrightarrow KCuO + Cu + \frac{1}{2} O_2$$

$$K + Cu_2O \longrightarrow KCuO + Cu$$

Reaction in a glass vessel produced the ternary oxide K_4CuO_3.

$$4K + 2CuO \xrightarrow{O_2} K_4CuO_3 + Cu$$

$$4K + Cu_2O \xrightarrow{O_2} K_4CuO_3 + Cu$$

This system parallels the potassium–nickel–oxygen system in that the lower oxidation state ternary oxide (in this case KCuO) is formed in the potassium containing the smallest amount of dissolved oxygen, *i.e.* in the nickel vessel, and the higher oxidation state ternary oxide (in this case K_4CuO_3) is formed in the potassium containing the largest amount of dissolved oxygen, *i.e.* in the glass vessel.

It is interesting to note that in the potassium–nickel–oxygen system the higher oxidation state ternary oxide K_2NiO_3 could not be obtained as a single phase in the series of solid state reactions studied. The compound K_2NiO_2 was always present. In the liquid potassium reactions carried out it was found that the two ternary oxides K_2NiO_2 and K_2NiO_3 were present in the products from both the nickel and glass vessels, although in differing amounts. In the potassium–copper–oxygen system the higher oxidation state ternary oxide K_4CuO_3 was obtained as a single phase in some of the solid state reactions studied. In the liquid potassium reactions carried out in this system only the low oxidation state ternary oxide KCuO or the high oxidation state ternary oxide K_4CuO_3 were obtained, depending on the type of vessel used. Therefore in both the nickel and copper systems there appears to be a direct correlation between the results obtained from the solid state reactions and those obtained from the reactions in liquid potassium. Bearing this correlation in mind a mechanism may be proposed for the reaction of the

copper oxides with liquid potassium. The compound KCuO is formed initially from the copper oxide.

$$K + Cu_2O \longrightarrow KCuO + Cu$$

The reaction proceeds no further unless the amount of dissolved oxygen present in the liquid potassium as potassium monoxide is sufficient to oxidize the KCuO to K_4CuO_3.

$$2K_2O + KCuO \longrightarrow K_4CuO_3 + K$$

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