# Reactions of Liquid Sodium with Transition-metal Oxides. Part IV.[1] Oxides of Iron, Cobalt, Nickel, and Copper

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The oxides of iron, cobalt, nickel, and copper are reduced by liquid sodium directly to the metal and sodium oxide. Only in the case of iron is a ternary oxide formed in the presence of an excess of liquid sodium. Solid-state reactions between sodium monoxide and the transition metals, carried out *in vacuo*, showed that reaction occurs at temperatures above 390° (Fe), 440° (Co), 480° (Ni), and 290° (Cu).

THE oxides used in this study have free energies of formation ($Fe_2O_3$, 59·1; $Fe_3O_4$, 60·8; FeO, 58·8; $Co_3O_4$, 45·5; NiO, 50·6; $Cu_2O$, 35·0; CuO, 29·0; *cf.* $Na_2O$, 89·9 kcal/g. atom at 298 K) which are appreciably less than that for sodium monoxide, and may thus be reduced by liquid sodium according to the general equation:

$$M_xO_y + 2y\text{Na} \longrightarrow xM + y\text{Na}_2\text{O}$$

The purpose of the present experiments was to determine whether this simple equation represented fully the behaviour of the oxides of iron, cobalt, nickel, and copper, in an excess of sodium, since any ternary oxide formation has significance in the corrosion of these metals when immersed in liquid sodium. The products of these reactions have been identified by (*a*) *X*-ray crystallographic examination of the products in a matrix of sodium, or (*b*) by distilling away the excess of sodium after reaction, followed by crystallographic examination of the remaining solid mixture. In the latter technique, the reaction products are inevitably subjected to vacuum and high temperature, and where ternary oxides may occur it is essential to determine whether they arose in the original reaction in an excess of sodium, or were formed during isolation from sodium. It was largely for this reason that the solid-state reactions of the transition metals with sodium monoxide were also studied.

There is already some evidence for ternary oxide formation in these systems. The compound $(Na_2O)_2FeO$ is formed by the reaction of iron with liquid sodium containing at least 1000 p.p.m. of oxygen,[2] but the compound $(Na_2O)NiO$ is not stable in the presence of liquid sodium.[3]

## EXPERIMENTAL

The general techniques used in the manipulation of sodium and reaction products have been described.[1] Transition-metal oxide (*ca.* 0·5 g) and sodium (7 g) were used in the reactions. The oxide was added in very small aliquots to the sodium contained in a nickel crucible, and stirred manually with a nickel spatula. Identification of reaction products without removal of sodium was achieved by extrusion, in an argon atmosphere, of a thin (0·45 mm diam.) wire of sodium taken from the reaction mixture after equilibration at either 400 or 600°. The wire was inserted into a standard Lindemann glass capillary tube (0·5 mm i.d.) which was sealed before removal from the argon-filled dry box in which all operations were carried out. The capillary tube was then mounted in an *X*-ray powder diffraction camera in the normal manner.

The oxide FeO was prepared by reaction of iron metal and the oxide $Fe_2O_3$ in equimolar proportions at 800° in an evacuated silica capsule. In order to prevent decomposition of the metastable oxide, FeO, the reaction mixture was quenched from 800° by liquid nitrogen. All other oxides used were of AnalaR grade and were dried to constant weight before reaction.

In the solid-state reactions, some experiments were carried out using synthetic mixtures of iron powder and sodium monoxide. In most cases, however, more suitable mixtures were available in the form of the products from the metal oxide–liquid sodium reactions. When such an experiment was completed, the sodium was distilled off *in vacuo*, and the product (which consisted largely, if

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[1] Part III, C. C. Addison, M. G. Barker, R. M. Lintonbon, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1969, 2457.

[2] P. Gross and G. L. Wilson, *J. Chem. Soc.* (*A*), 1970, **1913.**

[3] G. Woltersdorf, *Z. anorg. Chem.*, 1943, **252**, 126.

not entirely, of sodium oxide and the transition metal) was examined crystallographically. If the *X*-ray pattern gave no evidence of ternary oxide, the product could then be heated. The onset of reaction was indicated by evolution of sodium vapour. These mixtures had very small particle size and were intimately mixed, giving optimum conditions for solid-state reaction. The reaction temperatures observed are therefore likely to be lower than those obtained from mixtures of sodium monoxide with commercial metal powders.

## RESULTS AND DISCUSSION

### Iron

*Liquid Sodium Reactions.*—At temperatures below 400°, all the oxides of iron are reduced completely by liquid sodium to iron metal. *X*-Ray diffraction photographs of products extracted by vacuum distillation of sodium, and of reaction products retained in a matrix of sodium, showed only the diffraction lines of sodium oxide and iron metal. The relative intensities of the diffraction patterns of sodium oxide and iron in the products corresponded closely to the metal : oxygen ratio of the iron oxide (equations 1—3). Corresponding

$$Fe_2O_3 + 6Na \longrightarrow 2Fe + 3Na_2O \quad (1)$$

$$Fe_3O_4 + 8Na \longrightarrow 3Fe + 4Na_2O \quad (2)$$

$$FeO + 2Na \longrightarrow Fe + Na_2O \quad (3)$$

reactions at 600° gave products which contained not only metallic iron and sodium oxide, but also a third phase identified[2] as the compound $(Na_2O)_2FeO$. This compound was only present in the samples examined by the extrusion technique if the reaction mixture had been heated at temperatures greater than 500°, but ternary oxide formation is a function of oxygen concentration in the liquid sodium, rather than of temperature. At 600° the solubility of sodium oxide in liquid sodium is equivalent to 2730 p.p.m. oxygen in solution.[4] The sodium oxide in solution reacts with the metallic iron according to equation (4). As this reaction proceeds,

$$3Na_2O + Fe \longrightarrow (Na_2O)_2FeO + 2Na \quad (4)$$

some of the sodium oxide which has been formed as a separate phase in the initial reaction will go into solution to maintain the oxygen level in the solution. The sodium oxide : iron ratio in equation (4) would imply that all the sodium oxide generated by the initial reduction of the iron oxides, would be consumed in the formation of the compound $(Na_2O)_2FeO$. This is not so in the presence of liquid sodium since when the level of sodium oxide in solution falls below 1000 p.p.m., the compound $(Na_2O)_2FeO$ is not stable with respect to iron and sodium oxide,[2] and will no longer be formed. Thus, at equilibrium, there must always be at least 1000 p.p.m. oxygen in solution in the sodium, and the equilibrium state is represented by equation (5).

$$Na + Fe_2O_3 \longrightarrow Fe + (Na_2O)_2FeO + Na(O) \quad (5)$$

In the experiments reported here the quantity of oxide in solution represents *ca.* 5% of the weight of the reaction product. The *X*-ray powder diffraction patterns of the products showed the presence of sodium oxide in about this amount. At 400°, sodium is only capable of dissolving 402 p.p.m. oxygen;[4] at this concentration the compound $(Na_2O)_2FeO$ is unstable relative to sodium oxide and iron and has not been observed in the products of the 400° experiments.

*Solid-state Reactions.*—A series of solid-state experiments showed that sodium oxide reacts with iron metal at 390° *in vacuo*. At temperatures between 390 and 600° the compound $(Na_2O)_2FeO$ is formed; prolonged heating above 600° causes decomposition, with formation of the ferrite $NaFeO_2$.[2] The temperature at which the excess of sodium was distilled from the products in the liquid sodium–iron oxides reactions was deliberately chosen to be lower than 390°. The use of temperatures greater than 390° would obviously have led to the formation of the compound $(Na_2O)_2FeO$ during the sodium distillation stage.

### Cobalt

On mixing the oxide $Co_3O_4$ with solid sodium and heating the mixture, reaction occurred as soon as the sodium became molten. *X*-Ray powder diffraction patterns of the product of reaction showed the presence of sodium oxide with both the hexagonal form[5] and the cubic form[6] of cobalt metal. No ternary oxide of sodium and cobalt was observed, either in the presence of sodium, or after vacuum distillation at 280°. Sodium oxide did however react with cobalt metal *in vacuo* at 440° to form a red-brown solid, and sodium vapour was evolved. The *X*-ray powder diffraction pattern of the red-brown product showed it to contain unreacted cobalt metal together with a poorly crystalline (presumably ternary oxide) phase whose complex pattern (see Table) could not be identified.

### Nickel

Nickel oxide, NiO, reacted rapidly with liquid sodium at 150°, the oxide being reduced to nickel metal. No interaction between the metal and sodium oxide was observed in the presence of liquid sodium. The solid-state reaction between nickel and sodium oxide *in vacuo* commenced at 480°, and this high temperature precluded any interaction during sodium distillation. The product of the reaction of sodium oxide and nickel *in vacuo* above 480° contained unreacted nickel together with an unknown phase (Table) which may be the compound $(Na_2O)NiO$ reported by Woltersdorf.[3] No *X*-ray diffraction pattern was given for this compound so that no positive identification has yet been established.

### Copper

The oxides $Cu_2O$ and CuO are both reduced by liquid sodium at its melting point to copper metal and sodium

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[4] R. L. Eichelberger, U.S.A.E.C. Report AI-AEC-12685, 1968.

[5] L. J. E. Hofer and W. C. Peebles, *J. Amer. Chem. Soc.*, 1947, **69**, 897.

[6] Nat. Bur. Standards, Monograph **25**, 1965, section 4.

oxide. Sodium oxide reacts with copper at the relatively low temperature of 290° and ternary oxide formation is observed in products from which the excess of sodium has been removed by vacuum distillation at 300°. The extrusion technique shows that no double oxides were formed in the presence of sodium either at 400 or 600°. The ternary oxides were not identified; no correlation could be established between the $X$-ray diffraction patterns of the products (Table) and those reported for the compounds $NaCuO$,[7] $NaCuO_2$,[8] or $Na_3CuO_3$.[9] Different products were obtained by heating mixtures with the composition $Na_2O : Cu = 1 : 1$ and $1 : 2$, and these will be further investigated.

$X$-Ray diffraction patterns of the products of the reactions

| $d$(Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ | $d$ (Å) | $I/I_0$ |
|---|---|---|---|---|---|
| $4Na_2O + 3Co$ at 600° | | | | | |
| 5·27 | 70 | 2·73 | 5 | 2·35 | 90 |
| 4·15 | 30 | 2·64 | 70 | 1·97 | 70 |
| 3·85 | 40 | 2·54 | 90 | 1·58 | 60 |
| 3·50 | 50 | 2·47 | 100 | 1·49 | 5 |
| 3·31 | 40 | 2·40 | 90 | | |
| $Na_2O + Ni$ at 560° | | | | | |
| 6·85 | 10 | 2·59 | 30 | 2·097 | 40 |
| 5·71 | 10 | 2·54 | 20 | 1·918 | 20 |
| 4·64 | 10 | 2·413 | 100 | 1·707 | 10 |
| 4·33 | 70 | 2·358 | 20 | 1·650 | 10 |
| 4·17 | 50 | 2·311 | 20 | 1·534 | 10 |
| 4·06 | 30 | 2·280 | 20 | 1·442 | 20 |
| 2·85 | 10 | 2·167 | 40 | 1·411 | 20 |
| $Na_2O + 2Cu$ at 440° | | | | | |
| 6·46 | 5 | 2·447 | 5 | 1·547 | 25 |
| 5·68 | 40 | 2·352 | 100 | 1·504 | 5 |
| 4·59 | 80 | 2·288 | 90 | 1·485 | 10 |
| 4·04 | 100 | 2·048 | 5 | 1·371 | 25 |
| 3·55 | 20 | 1·992 | 5 | 1·339 | 5 |
| 3·22 | 30 | 1·909 | 10 | 1·208 | 5 |
| 3·09 | 10 | 1·877 | 5 | 1·147 | 5 |
| 2·996 | 5 | 1·835 | 5 | 1·072 | 5 |
| 2·831 | 60 | 1·697 | 20 | 1·025 | 5 |
| 2·666 | 10 | 1·649 | 15 | 1·007 | 5 |
| 2·569 | 100 | 1·617 | 20 | | |
| $Na_2O + Cu$ at 550° | | | | | |
| 6·52 | 50 | 2·377 | 100 | 1·429 | 10 |
| 4·55 | 5 | 2·300 | 15 | 1·349 | 30 |
| 4·03 | 25 | 2·248 | 10 | 1·341 | 30 |
| 3·84 | 30 | 2·165 | 30 | 1·318 | 5 |
| 3·57 | 95 | 1·923 | 60 | 1·293 | 5 |
| 3·32 | 25 | 1·880 | 20 | 1·207 | 10 |
| 3·02 | 10 | 1·839 | 10 | 1·189 | 5 |
| 2·714 | 60 | 1·686 | 30 | 1·178 | 5 |
| 2·614 | 60 | 1·551 | 10 | 1·145 | 10 |
| 2·574 | 10 | 1·486 | 10 | 0·942 | 5 |
| 2·515 | 10 | 1·442 | 10 | | |

*Correlation with Wetting Behaviour.*—In a study [10] of the contact angles for liquid sodium on surfaces of iron, cobalt, and nickel, critical temperatures were observed at which spreading of the sodium occurred. These temperatures were 140° (Fe), 190° (Co), and 195° (Ni), and the effect was attributed to the reduction, by sodium, of the oxide films present on the transition-metal surfaces at these temperatures. A full comparison between the behaviour of liquid sodium towards oxides in film form and oxides in bulk is restricted by the solidification of sodium below 98°. However, in all three cases films require higher temperatures for reaction than do the bulk oxides. This is reasonable, since the very thin films on polished metal surfaces are under the influence of the metallic substrate.

*Corrosion by Liquid Sodium.*—The conclusion from these experiments, which has direct significance in sodium corrosion, is that in the presence of a large excess of sodium, ternary oxides of sodium and the transition metal are only observed when the oxygen content of the sodium is very high, and then only in the case of iron. These oxygen concentrations are much higher than the range encountered in nuclear reactor coolants, so that ternary oxides play no significant part in the corrosion of these metals by liquid sodium.

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[7] R. Hoppe, K. Hestermann, and F. Schenk, *Z. anorg. Chem.*, 1969, **367**, 275.

[8] K. Hestermann and R. Hoppe, *Z. anorg. Chem.*, 1969, **367**, 261.

[9] K. Hestermann and R. Hoppe, *Z. anorg. Chem.*, 1969, **367**, 270.

[10] C. C. Addison, E. Iberson, and J. A. Manning, *J. Chem. Soc.*, 1962, 2699.