Reactions of Liquid Sodium with Transition-metal Oxides. Part V.[1] The Oxides Fe_3O_4, Co_3O_4, and NiO; stoicheiometry and reaction rates

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The stoicheiometry and rates of reaction of liquid sodium with the oxides Fe_3O_4, Co_3O_4, and NiO have been studied by measuring the quantity of sodium consumed over a range of reaction times and temperatures. The nickel oxide reaction becomes rapid above 150°, and the sodium consumed corresponds precisely to complete reduction to nickel metal. Reaction of Fe_3O_4 is slow below 250°; reduction to metallic iron is only 80% complete at 250°, and this is attributed to ternary oxide formation. The oxide Co_3O_4 reacts rapidly below 120°, and explosively above this temperature. Reduction to cobalt metal is about 90% complete at 120°.

THE oxides of iron, cobalt, and nickel are reduced by an excess of liquid sodium to the metals.[1] These oxides may also form ternary oxides with sodium monoxide,[2,3] the stability of which in the presence of an excess of sodium depends on the extent to which reactions such as (1) are thermodynamically favourable. The reactions described in the previous paper involved *ca.* 15 : 1 excess of sodium to metal oxide, and crystallographic examination of reaction products revealed the presence of the ternary oxide in the case of iron only.

$$2Na + (Na_2O)_2FeO \longrightarrow Fe + 3Na_2O + Na(O) \quad (1)$$

The purpose of the experiments now described was to determine whether ternary oxide formation influences the stoicheiometry, and the rate of reaction, of liquid sodium with oxides of these three metals. This was done by determining the quantities of sodium metal which remain in the mixture after the reactions had been allowed to proceed for measured times.

EXPERIMENTAL

The rate of reaction between a liquid metal and a solid oxide is necessarily a function of the extent to which reactants are brought into intimate contact. In the experiments described in the preceding paper, where small amounts of the oxide were spread on the surface of a much larger quantity of liquid sodium, reaction was no doubt more rapid. However, these conditions were not suitable for a study of stoicheiometry; for this reason the metal : oxide mole ratio has been reduced to about 2 : 1 and care taken to ensure similar stirring conditions. Comparisons of reaction rates with different oxides and at different temperatures are therefore comparable, though the rates themselves do not have fundamental significance.

Reaction vessels were made of Pyrex glass in the form of three-necked L-tubes (Figure 1). The foot of the L-tube was 11 cm long and 1·6 cm i.d., and carried two steel spheres A (0·75 cm diam.) to improve mixing. Sodium was contained in thin-walled glass capsules B (1 cm diam.) and was filtered at its melting point immediately before filling in an atmosphere of argon. The reaction tube fitted snugly into an aluminium block furnace C as shown, provided with resistance thermometer D giving temperature control to ±1°, and an observation window. The whole assembly was fitted into a rocking device by means of which the reaction tube could be rocked in a vertical plane through an angle of *ca.* 70° around the horizontal.

Procedure.—The metal oxide was dried at 110°, and cooled *in vacuo*. A weighed quantity (*ca.* 1 g), together with the steel spheres, were transferred into the sealed end of the reaction vessel. The sodium capsule (containing a known quantity, *ca.* 2 g, of metal) was then inserted as shown in Figure 1. During assembly, and throughout the experiment, the vessel was flushed with dry argon; this had the added advantage of preventing the sodium from inflaming in the event of fracture of the reaction vessel. Argon entered through E, and passed out through G and the loosely-fitting B14 stopper F. The sodium capsules were of such a length that they prevented stopper F from fitting completely into the socket. When the furnace achieved the required temperature, the stopper F was pressed home, thus breaking the capsule and liberating liquid sodium. Reaction times could be measured accurately, since the reactants did not mix until the tube was rocked.

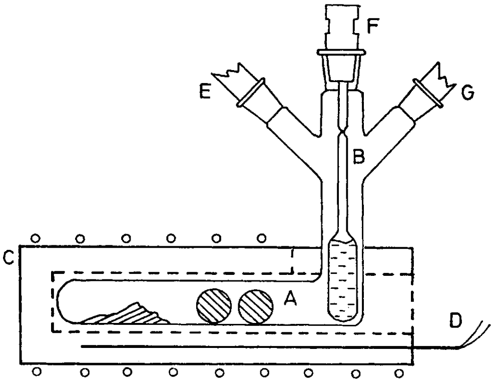

FIGURE 1 Reaction vessel

Determination of the Excess of Sodium.—This was calculated from the volume of hydrogen evolved on addition of water to the reaction vessel. After an appropriate time for reaction, the vessel was withdrawn from the furnace, E and G closed, and the vessel cooled in a stream of cold air. It was then attached to an assembly which allowed the addition of water slowly and collection of the hydrogen evolved. The sodium–water reaction was controllable within the reaction vessel so long as no oxygen was present to explode the hydrogen evolved, and so long as the temperature was not allowed to rise; a sodium hydroxide barrier is formed and the rate of reaction is governed by the rate of solution and diffusion of sodium hydroxide. During the addition of water, the reaction tube was immersed in a water-bath which was below room temperature; without these precautions, reaction was explosive. Water

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[1] Part IV, C. C. Addison, M. G. Barker, and A. J. Hooper, preceding paper.

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

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

(20 ml) was added dropwise, and 1—2 litres of hydrogen evolved. The assembly permitted initial evacuation before water addition. The measured volume of hydrogen was corrected for water-vapour pressure and temperature. In a series of blank calibration experiments carried out in the absence of transition-metal oxide, quantities of sodium in the range 0·2—2·0 g were determined with an accuracy of better than ±1%.

RESULTS AND DISCUSSION

Nickel Oxide.—For reaction (2) $-\Delta G_{400\text{K}} = 38{\cdot}1$ kcal mol^{-1}, so that the reaction is thermodynamically

$$2\text{Na} + \text{NiO} \longrightarrow \text{Na}_2\text{O} + \text{Ni} \qquad (2)$$

favourable, and in 1811 Gay Lussac reported that nickel was formed on heating sodium with nickel oxide.[4] A series of experiments was carried out at 120, 135, 150, and 175° in which the mixtures were allowed to react for varying times, the reaction stopped and the mixture analysed for residual sodium. Results are shown in Figure 2. The reproducibility of results is illustrated in the Table; in general, results became more reproducible as temperature and duration of reaction increased.

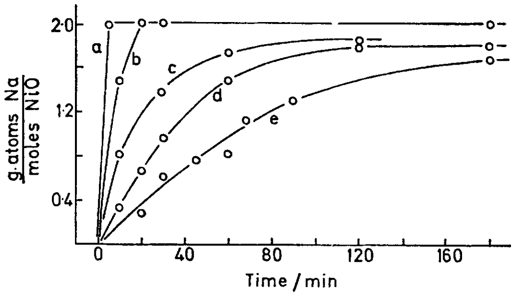

FIGURE 2 Reaction of liquid sodium with NiO; temperatures: a, 175°; b, 150°; c, 135° (oxide previously heated at 800°); d, 135°; e, 120°

Reproducibility of results at 135°
(using oxide preheated at 110°)

Duration of reaction (min)	30	60	120	180
g. atoms sodium used per mole of NiO	0·62	1·57	1·75	1·80
	1·13	1·33	1·86	1·85
	1·08	1·55	1·87	1·76

At the start of the reaction, the sodium was in the form of droplets which did not wet the glass. The glass surface then became wetted by sodium, giving a mirror surface, at times which decreased at higher temperatures (*ca.* 15, 8, 5 and <1 minutes at 120, 135, 150, and 175° respectively). The wetting is attributed to the sodium oxide produced in the reaction. Given efficient mixing, smooth reactions were observed. If mixing failed (*e.g.* was prevented by the broken capsule) local heating occurred, usually resulting in explosion. Products were usually hydrolysed for analysis, as described earlier. If exposed to the atmosphere, the dry product glowed and the sodium burned immediately; this is not characteristic of sodium alone, and is attributed to the presence of nickel in a finely divided, pyrophoric form.

The results in Figure 2 indicate that reaction is completed almost immediately at 175°, but is slow at 120°, and it is likely that a very slow reaction would take place at the melting point of sodium (98°). At 175°, sodium inflamed inside the reaction tube. Reaction products were analysed after 5 min contact at 175°; each mole of nickel oxide was found to have reacted with 1·99 g. atoms of sodium, in exact agreement with the simple equation (2) above. The black ferromagnetic powder could be isolated from the product after hydrolysis using a magnet, and identified as metallic nickel. There is therefore no evidence of the formation of any ternary oxide under these conditions, which is consistent with the crystallographic observations in the preceding paper. At 150°, reaction was less vigorous, and the sodium did not inflame. Reaction was complete after 20 min, and for reaction times of 20, 30, and 180 min, the g. atoms of sodium consumed per mole of nickel oxide present were 2·04, 2·05, and 1·98. Again, there is no evidence for ternary oxide formation. At 135 and 120° the sodium usage, within the several hours allowed, falls short of that required for full reduction to nickel metal; in view of the results at 175 and 150° this is attributed to inhibition by reaction products, and examination of the products gave no evidence of their consisting of other than nickel metal with a small amount of nickel oxide. The two curves for 135° (Figure 2) indicate that the rate of reaction is increased appreciably if nickel oxide is pre-dried at 800°, in spite of the fact that metal oxides are often less reactive after ignition. Thin films of sodium hydroxide are extremely cohesive, and can even prevent reaction of liquid sodium with water vapour.[5] Nickel oxide dried by the standard technique may contain adsorbed moisture which is insufficient to influence its behaviour to most reagents, but which may influence the reaction rate with sodium; this trace of moisture would be removed at 800°.

Iron Oxide.—For reaction (3) $-\Delta G_{400\text{K}} = 111{\cdot}1$

$$8\text{Na} + \text{Fe}_3\text{O}_4 \longrightarrow 4\text{Na}_2\text{O} + 3\text{Fe} \qquad (3)$$

kcal mol^{-1}, so that the forward reaction is favourable, and the formation of iron in this reaction has been reported.[4] The reaction is much slower than for nickel oxide under the same experimental conditions (compare Figures 2 and 3). At 250°, the rate of the reaction (Figure 3) for Fe_3O_4 is similar to that for NiO at 150° over the initial 60% of the reaction. The nickel oxide reaction proceeds to completion, but the iron oxide reaction ceases abruptly when only 6·5 of the 8 g. atoms of sodium required by reaction (3) have been used. (On hydrolysis of the product from the iron oxide reaction there was a slow, secondary evolution of hydrogen which is attributed to the reaction of finely divided iron with the alkaline solution.) Any of the oxide Fe_3O_4 which is converted into a ternary oxide [*e.g.* $(\text{Na}_2\text{O})_2\text{FeO}$] rather than being reduced to metal will require less

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[4] J. L. Gay Lussac and L. J. Thenard, *Rech. Phys. Chim., Paris*, 1811, **1**, 258, 264, 268, 273.

[5] C. C. Addison and J. A. Manning, *J. Chem. Soc.*, 1964, 4887.

sodium for the process, and in view of the observation in the preceding paper, it is reasonable to regard this cut-off in the Fe_3O_4 reduction process as due to the formation of a ternary oxide. In the presence of a large excess of liquid sodium, the oxide required for ternary oxide formation is provided *via* the oxygen dissolved in the liquid metal,[1] which is too dilute below 500°. In the present experiments the initial Na : Fe_3O_4 ratio is reduced to 2 : 1, so that the Na_2O–Fe solid–solid reaction (in which ternary oxide is produced above 390°) and reaction of sodium and iron oxides, become relevant. The use of a stirred, three-component system in which Na, Na_2O, and Fe_3O_4 are present in similar amounts appears to provide acceptable conditions for ternary oxide formation at temperatures lower than that required for the Na_2O–Fe reaction alone, or the Na–Fe_3O_4 reaction in the presence of an excess of sodium.

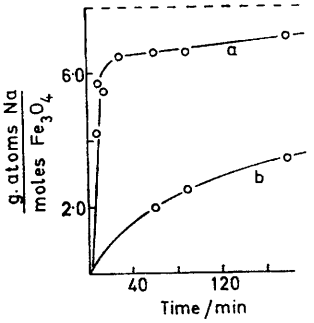

FIGURE 3 Reaction of liquid sodium with Fe_3O_4; temperatures: a, 250°; b, 150°

Cobalt Oxide.—The reaction (4) is favourable to the extent of $-\Delta G_{400K} = 172{\cdot}5$ kcal mol^{-1}. It occurs much more rapidly than in the case of the oxides NiO or

$$8Na + Co_3O_4 \longrightarrow 4Na_2O + 3Co \qquad (4)$$

Fe_3O_4; reaction rate curves are given in Figure 4 for 105 and 120°, and reaction is no doubt quite rapid at the melting point of sodium. Results for 120° lie on a smooth curve, but efficient mixing was essential. Mixtures frequently exploded at 105—120°, and above 120° they almost invariably exploded. The stoicheiometry of the reaction is intermediate between nickel and iron oxides. Reaction is rapid, yet the extent to which the sodium is consumed (7·4 g. atoms) falls short of the 8 g. atoms required in equation (4) by more than experimental error, and we assume that experimental conditions are suitable for the formation of some ternary oxide in this system.

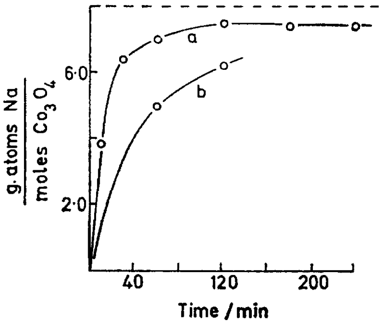

FIGURE 4 Reaction of liquid sodium with Co_3O_4; temperatures: a, 120°; b, 105°

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