Reactions of Liquid Sodium with Transition-metal Oxides. Part VIII.[1] The Oxides of Chromium-(III), -(IV), and -(VI) and Disodium Chromium(VI) Tetraoxide

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The reactions of the chromium oxides CrO_3, CrO_2, Cr_2O_3, and Na_2CrO_4 with liquid sodium have been studied at up to 600 °C, in some cases using differential thermal analysis. The reaction products have been examined by powder *X*-ray crystallography. The ternary oxide $NaCrO_2$ is formed in each case in which reaction took place, and this compound does not react further with dissolved oxygen in sodium up to the solubility limit. It is shown that the reaction of CrO_3 with liquid sodium does not yield Na_2CrO_3 as previously thought; this error is rationalised in terms of the experimental procedure, and improved techniques are identified.

THE behaviour of chromium in liquid-sodium environments is of considerable interest since chromium may be considered as the major alloying element in stainless steel which most readily participates in compound formation, and stainless steel is an established structural material for sodium-cooled fast-breeder reactors. Several studies (*e.g.* refs. 2 and 3) have shown that the oxide $NaCrO_2$ is formed when chromium-containing alloys are exposed to liquid sodium containing dissolved oxygen. Thermodynamic data of Gross *et al.*[4] and Jansson and Berkey[5] confirm the equilibrium between $NaCrO_2$ and solutions of oxygen in sodium. The reactions of the chromium oxides with liquid sodium are of particular relevance in this field since it has been shown[6] that ternary oxides produced from reactions of transition-metal oxides with

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[3] R. H. Hiltz, ' Corrosion by Liquid Metals,' eds. J. E. Draley and J. R. Weeks, Plenum, New York and London, 1970, p. 63.
[4] P. Gross, G. L. Wilson, and W. A. Gutteridge, *J. Chem. Soc.* (*A*), 1970, 1908.
[5] S. A. Jansson and E. Berkey, ref. 3, p. 479.
[6] C. C. Addison, M. G. Barker, and D. J. Wood, *J.C.S. Dalton*, 1972, 13.

sodium may also be formed in the corresponding corrosion system.

The reaction of CrO_3 with liquid sodium was previously thought [7] to yield a compound with the stoicheiometry Na_2CrO_3. It will be shown in this paper that this compound is not formed; the product obtained in the original experiments was a mixture of $NaCrO_2$ and the ternary oxide of Cr^{IV}, Na_4CrO_4, which was characterised in an earlier paper.[8]

EXPERIMENTAL

The techniques used in the reactions of liquid sodium with transition-metal oxides have been described previously.[9] The products of these reactions were examined by powder *X*-ray crystallography both in powder form, following removal of excess of sodium by vacuum distillation at 325 °C (5 × 10^{-5} mmHg),* and in the form of an extruded rod of excess of sodium containing the product.[10] The differential-thermal-analysis (d.t.a.) technique used to study the reactions was outlined previously.[7] The method of carrying out a reaction between stoicheiometric quantities of liquid sodium and a transition-metal oxide has also been described previously.[11]

Chromium(III) oxide and sodium chromate, Na_2CrO_4, were 'high-purity' grade, supplied by Johnson, Matthey. Chromium(IV) oxide was obtained from Radio Corporation of America. Chromium(VI) oxide was supplied by B.D.H. and purified as before.[7]

RESULTS AND DISCUSSION

Details of experimental conditions and reaction products are shown in the Table.

Reactions of chromium oxides with liquid sodium

Reactants	θ_e/°C	Products following extraction: (*i*) in extruded rod	(*ii*) by vacuum distillation
Cr_2O_3 + Na (excess)	450—600	$NaCrO_2$, Cr	$NaCrO_2$, Cr
CrO_2 + Na (excess)	300—600	$NaCrO_2$	$NaCrO_2$
CrO_3 + Na (excess)	150—600	$NaCrO_2$, Na_2O	$NaCrO_2$, Na_2O at 300, 325, and 400 °C; $NaCrO_2$, Na_4CrO_4 at 500 and 600 °C
Na_2CrO_4 + Na (excess)	150—600	$NaCrO_2$, Na_2O	$NaCrO_2$, Na_2O
Na_4CrO_4 + Na (excess)	600		$NaCrO_2$, Na_2O

Reactions.—Of chromium(III) *oxide.* Differential thermal analysis over the range 25—500 °C gave no indication of the temperature at which reaction occurs between Cr_2O_3 and liquid sodium. The reaction is not, therefore, highly exothermic. Examination, by powder *X*-ray diffraction, of the product remaining after heating Cr_2O_3–Na reaction mixtures to various temperatures showed that reaction does in fact occur between 400 and 450 °C. The powder *X*-ray diffraction pattern of the product from the reaction carried out at 450 °C was ill-defined, but a basically identical pattern with good definition of diffraction lines was obtained from the products of reactions carried out at higher temperatures (up to 600 °C). From the diffraction pattern of the reaction product it was deduced that reaction proceeds according to equation (1). The diffraction lines assigned

$$2Cr_2O_3 + 3Na \longrightarrow 3NaCrO_2 + Cr \quad (1)$$

to $NaCrO_2$ in the powder *X*-ray diffraction pattern of the reaction product were identical in *d* value and relative intensity to those published for $NaCrO_2$ by Gross *et al.*[4]

Of chromium(IV) *oxide.* The sole product of the reaction between CrO_2 and liquid sodium was sodium chromium(III) dioxide.

$$Na + CrO_2 \longrightarrow NaCrO_2 \quad (2)$$

Of the oxides CrO_3 *and* Na_2CrO_4. Differential thermal analysis of the reaction between the oxide CrO_3 and liquid sodium has been reported previously.[7] This showed that an extremely exothermic reaction occurs at the melting point of sodium.

In the present work the reaction products $NaCrO_2$ and Na_2O were formed in all reactions equilibrated between 150 and 600 °C where sodium was initially present in appreciable excess over the 3 : 1 Na : CrO_3 molar ratio demanded by reaction (3). Similarly the products of

$$CrO_3 + 3Na \longrightarrow NaCrO_2 + Na_2O \quad (3)$$

reactions between sodium chromate, Na_2CrO_4, and sodium, equilibrated at temperatures in this same range, were identified, by powder *X*-ray analysis, as $NaCrO_2$ and sodium mono-oxide, Na_2O. It is deduced that the reaction proceeds as in equation (4).

$$Na_2CrO_4 + 3Na \longrightarrow NaCrO_2 + 2Na_2O \quad (4)$$

The conditions under which these reactions of CrO_3 and Na_2CrO_4 were performed were such that the quantities of Na_2O generated would give a saturated solution of oxygen in the sodium. These reactions have shown, therefore, that the ternary oxide $NaCrO_2$ is stable, up to 600 °C, in liquid sodium containing dissolved Na_2O up to the solubility limit, and will not react with dissolved oxygen to give further ternary oxides. This contrasts with the solid-state reaction between $NaCrO_2$ and Na_2O which yields [8] the ternary oxide Na_4CrO_4 at 410 °C.

Formation of Na_4CrO_4.—The instability in liquid sodium of the ternary oxide Na_4CrO_4 containing Cr^{IV} was further demonstrated by adding the compound to high-purity liquid sodium and equilibrating the reaction mixture at 600 °C. The reaction product remaining after removal of excess of sodium by vacuum distillation

* 1 mmHg ≈ 13.6 × 9.8 Pa.

[7] C. C. Addison and M. G. Barker, *J. Chem. Soc.*, 1965, 5534.
[8] M. G. Barker and A. J. Hooper, *J.C.S. Dalton*, 1975, 2487.
[9] C. C. Addison, M. G. Barker, and R. J. Pulham, *J. Chem. Soc.*, 1965, 4483.
[10] C. C. Addison, M. G. Barker, and A. J. Hooper, *J.C.S. Dalton*, 1972, 1017.
[11] M. G. Barker and A. J. Hooper, *J.C.S. Dalton*, 1973, 1520.

at 325 °C was shown, by powder *X*-ray analysis, to consist of $NaCrO_2$ and Na_2O [equation (5)].

$$Na_4CrO_4 + Na \longrightarrow NaCrO_2 + 2Na_2O \quad (5)$$

The compound Na_4CrO_4 may be obtained from a reaction mixture containing liquid sodium using the stoicheiometric quantities of CrO_3 and sodium demanded by equation (3). The black-green granular product of this reaction was shown, by powder *X*-ray analysis, to contain the compounds Na_4CrO_4 and $NaCrO_2$ and free sodium [equation (6)]. Clearly, in this reaction the

$$CrO_3 + 3Na \longrightarrow \tfrac{1}{2}NaCrO_2 + \tfrac{1}{2}Na_4CrO_4 + \tfrac{1}{2}Na \quad (6)$$

sodium reacts initially with CrO_3 to yield a 1 : 1 $NaCrO_2$–Na_2O mixture as in equation (3). The solid-state reaction described in ref. 8 then occurs to give Na_4CrO_4 and sodium [equation (7)].

$$NaCrO_2 + Na_2O \longrightarrow \tfrac{1}{2}Na_4CrO_4 + \tfrac{1}{2}Na + \tfrac{1}{2}NaCrO_2 \text{ (unchanged)} \quad (7)$$

Solid-state reactions between chromium metal and Na_2O have been shown to yield Na_4CrO_4.[8] In contrast, intimate mixtures of chromium metal powder and Na_2O in liquid sodium gave $NaCrO_2$ and unchanged starting materials.

Vacuum Distillation.—The solid-state reactions of Na_2O with chromium and with $NaCrO_2$ are initiated at 370 and 410 °C respectively.[8] In studies of the sodium–chromium–oxygen system, therefore, vacuum distillation to remove excess of sodium from reaction products must be conducted at temperatures below these, to preclude possible interactions of the products.

In an earlier study,[7] the product of the reaction between CrO_3 and sodium was identified as the ternary oxide containing Cr^{IV}, Na_2CrO_3. One of the factors which may have led to this error was that excess of sodium was removed from the reaction product by vacuum distillation at 450 °C, a temperature high enough for further interaction to have taken place *in vacuo* between the $NaCrO_2$ and Na_2O in the reaction product, as in equation (7).

Examination of the *X*-ray diffraction pattern published for Na_2CrO_3 reveals that all the diffraction lines given by the sample from the reaction of sodium with CrO_3 at 450 °C, and all but four of the diffraction lines given by the sample from the reaction at 600 °C, can be assigned to $NaCrO_2$. No diffractions could be assigned to either Na_4CrO_4 formed during vacuum distillation or to unchanged Na_2O. This probably indicates that poorly crystalline Na_4CrO_4 had been formed; the chemical analyses of the final products demonstrate that further reaction (between $NaCrO_2$ and Na_2O) occurred during distillation.

In order to confirm this hypothesis, reactions of CrO_3 with sodium were carried out at 600 °C and the excess of sodium was removed by vacuum distillation at 300, 400, 500, and 600 °C. The products from distillation at 300 and 400 °C were $NaCrO_2$ and Na_2O, whereas at the higher temperatures Na_2O was no longer present but a very poor diffraction pattern for Na_4CrO_4 was obtained in addition to the well resolved pattern of $NaCrO_2$.

Conclusion.—Whilst Gross *et al.*[4] carried out experiments using sodium vapour to demonstrate that $NaCrO_2$ is the only ternary oxide which is stable in contact with chromium and liquid sodium, the present work confirms this result by experiments involving liquid sodium. It has been shown also that $NaCrO_2$ will not react at temperatures up to 600 °C with oxygen dissolved in sodium even when the dissolved oxygen is at saturation level with respect to Na_2O.

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