

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 Berkey⁵ 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 shown⁶ that ternary oxides produced from reactions of transition-metal oxides with

¹ Part VII, M. G. Barker, A. J. Hooper, and D. J. Wood, *J.C.S. Dalton*, 1974, 55.

² A. W. Thorley and C. Tyzack, *Proc. Symp. Alkali-metal Coolants*, IAEA, Vienna, November 1966, p. 97.

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 thought⁷ to yield a compound with the stoichiometry 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 stoichiometric 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

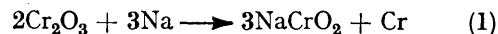
Details of experimental conditions and reaction products are shown in the Table.

Reactions of chromium oxides with liquid sodium

Reactants	$\theta_0/^\circ\text{C}$	Products following extraction	
		(i) in extruded rod	(ii) by vacuum distillation
$\text{Cr}_2\text{O}_3 + \text{Na}$ (excess)	450—600	NaCrO_2 , Cr	NaCrO_2 , Cr
$\text{CrO}_2 + \text{Na}$ (excess)	300—600	NaCrO_2	NaCrO_2
$\text{CrO}_3 + \text{Na}$ (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
$\text{Na}_2\text{CrO}_4 + \text{Na}$ (excess)	150—600	NaCrO_2 , Na_2O	NaCrO_2 , Na_2O
$\text{Na}_4\text{CrO}_4 + \text{Na}$ (excess)	600		NaCrO_2 , Na_2O

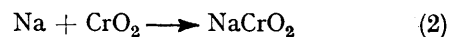
Reactions.—Of chromium(III) oxide. Differential thermal analysis over the range 25 — 500°C gave no indication of the temperature at which reaction occurs between Cr_2O_3 and liquid sodium. The reaction is not, therefore, highly exothermic. Examination, by powder X -ray diffraction, of the product remaining 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



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.

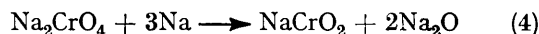


Of the oxides CrO_3 and Na_2CrO_4 . Differential thermal analysis of the reaction between the oxide CrO_3 and liquid sodium has been reported previously.⁷ This showed that an extremely exothermic reaction occurs at the melting point of sodium.

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:CrO₃ molar ratio demanded by reaction (3). Similarly the products of



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).



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 yields⁸ 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 $\approx 13.6 \times 9.8$ Pa.

⁷ C. C. Addison and M. G. Barker, *J. Chem. Soc.*, 1965, 5534.

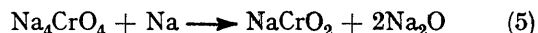
⁸ M. G. Barker and A. J. Hooper, *J.C.S. Dalton*, 1975, 2487.

⁹ C. C. Addison, M. G. Barker, and R. J. Pulham, *J. Chem. Soc.*, 1965, 4483.

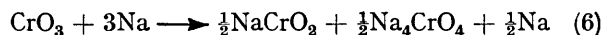
¹⁰ C. C. Addison, M. G. Barker, and A. J. Hooper, *J.C.S. Dalton*, 1972, 1017.

¹¹ M. G. Barker and A. J. Hooper, *J.C.S. Dalton*, 1973, 1520.

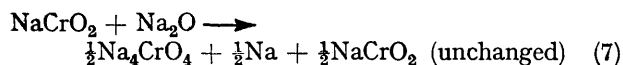
at 325 °C was shown, by powder X-ray analysis, to consist of NaCrO₂ and Na₂O [equation (5)].



The compound Na₄CrO₄ may be obtained from a reaction mixture containing liquid sodium using the stoichiometric quantities of CrO₃ 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 Na₄CrO₄ and NaCrO₂ and free sodium [equation (6)]. Clearly, in this reaction the



sodium reacts initially with CrO₃ to yield a 1 : 1 NaCrO₂-Na₂O mixture as in equation (3). The solid-state reaction described in ref. 8 then occurs to give Na₄CrO₄ and sodium [equation (7)].



Solid-state reactions between chromium metal and Na₂O have been shown to yield Na₄CrO₄.⁸ In contrast, intimate mixtures of chromium metal powder and Na₂O in liquid sodium gave NaCrO₂ and unchanged starting materials.

Vacuum Distillation.—The solid-state reactions of Na₂O with chromium and with NaCrO₂ 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 CrO₃ and sodium was identified as the ternary oxide containing Cr^{IV}, Na₂CrO₃. 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 NaCrO₂ and Na₂O in the reaction product, as in equation (7).

Examination of the X-ray diffraction pattern published for Na₂CrO₃ reveals that all the diffraction lines given by the sample from the reaction of sodium with CrO₃ 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 NaCrO₂. No diffractions could be assigned to either Na₄CrO₄ formed during vacuum distillation or to unchanged Na₂O. This probably indicates that poorly crystalline Na₄CrO₄ had been formed; the chemical analyses of the final products demonstrate that further reaction (between NaCrO₂ and Na₂O) occurred during distillation.

In order to confirm this hypothesis, reactions of CrO₃ 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 NaCrO₂ and Na₂O, whereas at the higher temperatures Na₂O was no longer present but a very poor diffraction pattern for Na₄CrO₄ was obtained in addition to the well resolved pattern of NaCrO₂.

Conclusion.—Whilst Gross *et al.*⁴ carried out experiments using sodium vapour to demonstrate that NaCrO₂ 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 NaCrO₂ 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 Na₂O.

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