Reactions of Chromium Oxides and Chromium Metal with Disodium Oxide

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The ternary oxides $NaCrO_2$, Na_3CrO_4, and Na_4CrO_4 are characterised by *X*-ray powder-diffraction patterns. The compound $NaCrO_2$ has been prepared from equimolar quantities of Na_2O and Cr_2O_3, but Na_4CrO_4 is formed at higher concentrations of Na_2O or from reaction of Na_2O and Cr. The ternary oxide $NaCrO_2$ decomposes reversibly to simple oxides at *ca.* 795 °C.

AN understanding of the sodium–chromium–oxygen phase system is of great value to considerations of the compatibility of chromium-bearing alloys with aggressive media such as oxygen-contaminated sodium, sodium–water reaction products, molten sodium hydroxide, or sodium hydroxide solutions. Therefore, we have conducted a study of solid-state reactions in order to characterise the stable compounds in some sections of the quaternary Na_2O, Cr_2O_3, CrO_2, and CrO_3 diagram. Reactions of Na_2O with Cr_2O_3, CrO_2, CrO_3, $Na_2[CrO_4]$, and Cr metal have been investigated and the reaction products identified. Previous investigations on this phase system have tended to concentrate on the preparation of a single compound. We have attempted to cover a variety of synthesis reactions in order to gain an insight into the range of stoicheiometries which may be found for a particular oxidation state.

RESULTS AND DISCUSSION

Details of reaction conditions and the products and their structures are given in Table 1.

TABLE 1

Reactions of chromium oxides with disodium oxide

Reaction	Reactants	Conditions	Product	Structure
(1)	$Na_2O + Cr_2O_3$	400—600 °C, under argon or *in vacuo*	$NaCrO_2$	Hexagonal, α-$NaFeO_2$ type: $a = 2.968$, $c = 15.94$ Å
(2)	$NaCrO_2 + 2Na_2O$	410 °C, *in vacuo*	Na_4CrO_4 (+Na)	Orthorhombic: $a = 11.460$, $b = 13.431$, $c = 9.993$ Å
(3)	$Na_2O + CrO_2$	350—600 °C, dynamic or sealed, argon or *in vacuo*	$NaCrO_2$ mainly, Na_4CrO_4, Na_3CrO_4, $Na_2[CrO_4]$	
(4)	$Na_2[CrO_4] + 1.05\ NaN_3$	320 °C, then to 330 °C at 1 °C h^{-1}, finally anneal for 24 h at 800 °C under a dry oxygen-free nitrogen stream	Na_3CrO_4 (+N_2)	Cubic, Na_2CaSiO_4 type: $a = 7.60$ Å
(5)	$Na_2[CrO_4] + Na_2O$	As reaction (3)	Na_3CrO_4 (+O_2)	Cubic, Na_2CaSiO_4 type

Reactions of Chromium(III) *Oxide*.—Syntheses of $NaCrO_2$ [Table 1, reaction (1)] gave a dull green product having the structure described by Gross *et al.*[1] The structure of $NaCrO_2$ at low temperature was examined by powder *X*-ray crystallography. The structure of the compound (at −100 °C) remained unchanged from the hexagonal room-temperature form (Table 1) and the line splittings evident in the powder-diffraction pattern of $NaVO_2$ at low temperature[2] were not observed for $NaCrO_2$. A high-temperature *X*-ray study on the compound showed that the hexagonal structure was stable at temperatures up to 792 °C, at which decomposition to Na_2O and Cr_2O_3 occurred. A parallel differential thermal analysis (d.t.a.) experiment confirmed the decomposition temperature, which was observed as a single endothermic transition at 795 °C being reversible on cooling.

A $NaCrO_2$–Na_2O mixture (1 : 2 mol ratio) heated *in vacuo* (2×10^{-5} mmHg) † reacted at 410 °C, with evolution of sodium [Table 1, reaction (2)]. The deep green product, remaining after reaction was complete, gave an *X*-ray powder-diffraction pattern closely resembling the line diagram by Bunsen[3] to represent the diffraction pattern of Na_4CrO_4. Furthermore, the weight loss of the reaction mixture corresponded very closely to evolution of 1 mol of sodium according to equation (i)

$$NaCrO_2(c) + 2Na_2O(c) \xrightarrow{410\ °C} Na_4CrO_4(c) + Na(g) \quad \text{(i)}$$

(Found: weight loss, 9.90. Calc.: 9.95%). Estimation of the sodium evolved, which distilled on to the cooler parts of the silica reaction tube, showed that ⩾98% of the weight loss was in the form of this distillate. Clearly $NaCrO_2$ reacts with Na_2O *in vacuo* at 410 °C to give the ternary oxide Na_4CrO_4. We have shown, in a series of reactions of oxides with liquid sodium,[4] that reaction of Na_4CrO_4 with liquid sodium at 410 °C yields $NaCrO_2$ and Na_2O as products. Clearly, for reaction (i) the free-energy change is positive and Na_4CrO_4 will only be produced where the sodium has an activity less than unity, as in our synthesis *in vacuo*. Taking the known free energies of formation of $NaCrO_2$ (ref. 1) and Na_2O (ref. 5) at this temperature, the free energy of formation of the compound Na_4CrO_4 at 410 °C, ΔG_f-(410 °C), is greater than −1 378 kJ mol^{-1}.

The *X*-ray powder-diffraction pattern of Na_4CrO_4 is shown in Table 2. The pattern may be indexed on the

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† 1 mmHg ≈ 13.6 × 9.8 Pa.

[1] P. Gross, G. L. Wilson, and W. A. Gutteridge, *J. Chem. Soc.* (*A*), 1970, 1908.

[2] M. G. Barker and A. J. Hooper, *J.C.S. Dalton*, 1973, 1517.

[3] H. Bunsen, Dissertation, Karlsruhe, 1957.

[4] M. G. Barker and A. J. Hooper, unpublished work.

[5] C. E. Wicks and F. E. Block, Bureau of Mines Bulletin 605, 1963.

basis of an orthorhombic structure with cell constants $a = 11.460$, $b = 13.431$, and $c = 9.993$ Å and is isostructural with the titanium and vanadium analogues, Na_4TiO_4 (ref. 6) and Na_4VO_4 (ref. 7). A recent study[8] has shown that these compounds may be isostructural with Na_4SiO_4 and have a triclinic unit cell.[9] The cell parameters of Na_4CrO_4 based on the triclinic cell are $a = 5.71$, $b = 8.60$, and $c = 6.38$ Å and $\alpha = 98.20$, $\beta = 123.4$, and $\gamma = 99.10°$.

TABLE 2

X-Ray diffraction pattern of Na_4CrO_4

d/Å	hkl	I/I_0	d/Å	hkl	I/I_0
5.306	210	20	2.368	043	100
4.983	121	85	2.333	323	90
4.529	102	50	2.222	501	95
4.331	220	30	2.161	333	10
4.057	031	12	2.103	260	20
3.849	131	50	1.981	531	5
3.562	212	45	1.953	115	2
3.292	032	15	1.794	523	4
3.165	103	30	1.722	370	3
3.100	113	3	1.695	145	5
2.940	312	5	1.672	363	5
2.731	401	50	1.653	164	20
2.667	033	85	1.631	116	10
2.636	223	95	1.616	701	5
2.536	151	8	1.597	281	10
2.449	341	3	1.575	182	15

The results of this study have been corroborated by Lavielle *et al.*[10] in a study of the reactions of Cr_2O_3 with Na_2O (also Li_2O).

Reaction of Chromium(IV) *Oxide*.—Preparation of the ternary oxide Na_2CrO_3 containing Cr^{IV} and sodium was attempted by Scholder and Schwarz.[11] However, these workers only obtained equimolar proportions of the ternary oxides $NaCrO_2$ and Na_3CrO_4. This result is analogous to our previous observations on the Na_2O–VO_2 (1 : 1) reaction[2] and it seemed likely that equimolar quantities of Na_2O and CrO_2 would react according to equation (ii). However, a number of experiments

$$Na_2O + CrO_2 \longrightarrow 0.5NaCrO_2 + 0.5Na_3CrO_4 \quad \text{(ii)}$$

[Table 1, reaction (3)] all yielded $NaCrO_2$ as the principal product with smaller quantities of Na_4CrO_4, Na_3CrO_4 (see next section), and $Na_2[CrO_4]$ in varying proportions. These observations suggest that equilibrium is not attained readily in this reaction and that the CrO_2 may lose oxygen prior to reaction.

Formation of the Compound Na_3CrO_4. The poor thermal stability of Cr_2O_5 precludes any direct reaction with Na_2O. The work of Scholder and Schwarz[11] showed that several methods may be employed for the preparation of the compound Na_3CrO_4. The best synthesis route appears to be reaction of anhydrous $Na_2[CrO_4]$ with sodium azide [Table 1, reaction (4)].

The powder X-ray diffraction pattern of the dark green reaction product is shown in Table 3. Chemical analysis was carried out to confirm that the dark green product was indeed Na_3CrO_4. The compound dissolved in dilute sulphuric acid to give a yellow-green solution, which suggested the presence of a mixture of Cr^{VI} and Cr^{III}. Treatment of this solution with sulphur dioxide reduced all the chromium present to the oxidation state III. The chromium was then estimated as Cr^{III} using an atomic-absorption spectrophotometer (Southern Analytical, model A3000). Reference solutions of Cr^{III} were obtained by sulphur-dioxide reduction of a standardised, acidified, potassium dichromate solution and subsequent dilutions of the resulting Cr^{III} solution. Sodium was estimated with a flame photometer (Found: Cr, 28.3; Na, 37.0. Calc. for Na_3CrO_4: Cr, 28.1; Na, 37.3%). In addition, the Cr^{VI} present in the yellow-green solution obtained on dissolving the reaction product in dilute acid was estimated: an aliquot portion of the solution was added to a known excess of standardised ammonium iron(II) sulphate solution and the excess of Fe^{2+} was then titrated against standardised potassium permanganate solution (Found: Cr^{VI}, 18.9% of initial sample weight. Calc. for 3 : 2 ratio in solution of total chromium: Cr^{VI}, 18.7%).

TABLE 3

X-Ray diffraction pattern of Na_3CrO_4

d/Å	hkl	I/I_0	d/Å	hkl	I/I_0
4.373	111	90	1.704	420	5
3.784	200	40	1.556	422	20
2.682	220	100	1.467	333	10
2.298	311	15	1.351	440	5
2.161	222	5	1.287	531	5
1.903	400	25	1.207	620	8
1.749	331	10			

These analysis figures confirm that the dark green reaction product is Na_3CrO_4, and further show that in acid solution the compound undergoes disproportionation as in (iii). The compound is isostructural with γ-Na_3VO_4 which we have reported previously[12] and has a

$$3[CrO_4]^{3-} + 10H^+ \longrightarrow [Cr_2O_7]^{2-} + Cr^{3+} + 4H_2O \quad \text{(iii)}$$

Na_2CaSiO_4-type cubic structure with $a = 7.60$ Å. Since this work was carried out a further preparation of the compound has been reported,[13] using reaction (iv).

$$5Na_2O + Cr_2O_3 + 4Na_2[CrO_4] \longrightarrow 6Na_3CrO_4 \quad \text{(iv)}$$

The product of this reaction also yielded a cubic phase with the cell dimension $a = 7.61 \pm 0.01$ Å. Therefore, it seems conclusive that the compound Na_3CrO_4 falls into the series of isostructural cubic phases Na_3MO_4 [M = V (ref. 12), Cr, or Mn (ref. 4)].

Reaction of Chromium(VI) *Oxide*.—The familiar compounds sodium chromate, $Na_2[CrO_4]$, and sodium dichromate, $Na_2[Cr_2O_7]$, are readily prepared by reactions between Na_2O and CrO_3 in 1 : 1 and 1 : 2 mol

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[6] M. G. Barker and D. J. Wood, *J.C.S. Dalton*, 1972, 2448.

[7] M. G. Barker and A. J. Hooper, *J.C.S. Dalton*, 1973, 1520.

[8] R. Olazcuaga, Ph.D. Thesis, University of Bordeaux I, 1974.

[9] K. Kantz, G. Muller, and W. Schneider, *Glass Ber.*, 1970, **43**, 377.

[10] L. Lavielle, H. Kessler, and A. Hatterer, *Bull. Soc. chim. France*, 1973, 1918.

[11] R. Scholder and H. Schwarz, *Z. anorg. Chem.*, 1963, **1**, 1 and refs. therein.

[12] M. G. Barker and A. J. Hooper, *J.C.S. Dalton*, 1973, 1513.

[13] G. Le Flem, R. Olazcuaga, J.-P. Parant, J.-M. Reau, and C. Fouassier, *Compt. rend.*, 1971, **C273**, 1358.

ratios respectively. However, the ternary oxide of general formula Na_4MO_5, which has been obtained for $M = Mo$ or W,[14] has not been prepared in the chromium system. Consequently reaction (5) (Table 1) was investigated. The products were invariably unchanged $Na_2[CrO_4]$ and Na_2O, and varying quantities of Na_3CrO_4 (having the Na_2CaSiO_4-type cubic structure). This indicated partial reaction of the type (v).

$$Na_2[CrO_4] + \tfrac{1}{2}Na_2O \longrightarrow Na_3CrO_4 + \tfrac{1}{4}O_2\uparrow \qquad \text{(v)}$$

Reaction of Chromium Metal.—Disodium oxide and chromium metal were heated, in the form of intimately mixed powders, to 600 °C *in vacuo*. The chromium metal powder used had previously been sieved through a 300 mesh sieve. Sodium evolution was observed at *ca.* 370 °C from all the reaction mixtures. The reaction products in addition to sodium were identified by *X*-ray powder diffraction (Table 4).

TABLE 4

Reactions of Na_2O with chromium metal

Expt. no.	Na_2O : Cr	Products
(1)	1 : 1	Na_4CrO_4, Cr, Na
(2)	2 : 1	Na_4CrO_4, Cr, Na
(3)	3 : 1	Na_4CrO_4, Cr, Na
(4)	4 : 1	Na_4CrO_4, Na

The compound $NaCrO_2$ may have been present in small quantities in the products from experiments (1)—(3) but positive identification was impossible since the two lines of appreciable intensity in the *X*-ray powder-diffraction pattern of $NaCrO_2$ (at $d = 5.31$ and 2.166 Å) coincide with lines in that of Na_4CrO_4. Clearly the favoured overall reaction is (vi) but reaction may well

$$4Na_2O + Cr \longrightarrow Na_4CrO_4 + 4Na \qquad \text{(vi)}$$

proceed by a stepwise mechanism [equations (vii) and (viii)].

$$2Na_2O + Cr \longrightarrow NaCrO_2 + 3Na \qquad \text{(vii)}$$

$$NaCrO_2 + 2Na_2O \longrightarrow Na_4CrO_4 + Na \qquad \text{(viii)}$$

EXPERIMENTAL

Reagents.—Disodium oxide was prepared as described previously.[15] Sodium azide of ⩾99% purity was supplied by B.D.H. Chromium(III) oxide and sodium chromate, $Na_2[CrO_4]$, 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.[16] Chromium metal powder of ⩾99.98% purity was supplied by Hopkin and Williams.

The methods used for the solid-state reactions of Na_2O with transition metals and their oxides are described in ref. 15. The d.t.a. apparatus used was decribed in ref. 12. High-temperature *X*-ray diffraction patterns were obtained using a Nonius high-temperature Guinier–Lenne camera. Low-temperature patterns were obtained using a Philips 114.83 mm camera modified such that the sample was bathed in a stream of nitrogen gas which had been previously cooled by passage through liquid nitrogen.

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[14] J.-M. Reau, P. Hagenmuller, and C. Fouassier, *Bull. Soc. chim. France*, 1967, 3873.

[15] M. G. Barker and D. J. Wood, *J.C.S. Dalton*, 1972, 9.

[16] C. C. Addison and M. G. Barker, *J. Chem. Soc.*, 1965, 5534.