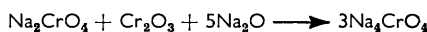


**1032. Reactions of Liquid Sodium with Transition-metal Oxides. Part II.<sup>1</sup> Reduction of Chromium Trioxide to a Ternary Oxide of Chromium(IV)**

By C. C. ADDISON and M. G. BARKER

Chromium trioxide reacts with liquid sodium at temperatures near the melting point of sodium, to give a single product, which is a highly hygroscopic green powder of composition  $\text{Na}_2\text{CrO}_3$ . The argument for the chromium(IV) oxidation state is supported by its disproportionation to chromate(VI) and chromium(III) oxide on contact with water, and by its magnetic susceptibility. It gives green solutions in molten lithium chloride-potassium chloride eutectic, but is oxidised immediately in molten nitrates. No chemical decomposition occurs at temperatures up to  $600^\circ$ , but on prolonged heating at  $600^\circ$  further line-splitting is observed in the X-ray diffraction pattern obtained at lower temperatures. The diffraction pattern is indexed on the basis of a monoclinic unit cell, dimensions for which are recorded.

In Part I<sup>1</sup> it was shown that the products of reactions between liquid sodium and molybdenum or tungsten dioxide consisted of the transition metal together with the ternary oxide,  $\text{Na}_3\text{M}_2\text{O}_6$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ); the production of a stoichiometric mixture of metal and ternary oxide is also observed with a number of other transition-metal oxides, including the trioxides of molybdenum and tungsten. The product of reaction of chromium trioxide is unusual in three respects: firstly, it is a single ternary-oxide phase,  $\text{Na}_2\text{CrO}_3$ , which does not undergo disproportionation even at  $600^\circ$ ; secondly, this product is a compound of chromium(IV), and illustrates the high stability of this oxidation state in the absence of water. Compounds of chromium(IV) oxide are still relatively rare. The oxide  $\text{CrO}_2$  itself is known,<sup>2</sup> and the green compound  $\text{Ba}_2\text{CrO}_4$  has been prepared by reaction of barium chromate(VI) with barium hydroxide,<sup>3</sup> its magnetic moment (2.82 B.M.) is consistent with the chromium(IV) oxidation state in this compound.<sup>4</sup> The presence of chromium(IV) species in solutions of potassium chromate(VI) in molten potassium hydroxide has also been suggested.<sup>5</sup> Scholder<sup>6</sup> has reported the preparation of a ternary oxide  $\text{Na}_4\text{CrO}_4$  by the reaction



but attempts to isolate the compound  $\text{Na}_2\text{CrO}_3$  by the use of the same reactants in different proportions were unsuccessful.<sup>6</sup> Finally, salts having the metachromate formula  $\text{CrO}_3^{n-}$  are much less familiar than those of the orthochromate unit  $\text{CrO}_4^{n-}$ . The compound  $\text{SrCrO}_3$  mentioned by Yakel<sup>7</sup> appears to be the only compound resembling the product described in this Paper, though compounds  $\text{MCr}^{\text{III}}\text{O}_3$  ( $\text{M} = \text{an early lanthanide element}$ ) have been described.<sup>8</sup>

#### EXPERIMENTAL

The experimental techniques used in liquid sodium-metal oxide reactions have already been described.<sup>1</sup> Pure chromium trioxide (about 0.5 g., dried *in vacuo* at  $130^\circ$ ) was added to 5 ml. of liquid sodium (at about  $150^\circ$ ) in a nickel crucible, which was held in an argon-filled glove box. An immediate, vigorous reaction caused the remaining chromium trioxide (m. p.  $196^\circ$ ) to melt, whereupon the reaction became violent. The green reaction product was not wetted by the

<sup>1</sup> C. C. Addison, M. G. Barker, and R. J. Pulham, *J.*, 1965, 4483.

<sup>2</sup> K. A. Wilhelmi and O. Jonsson, *Acta Chem. Scand.*, 1958, **12**, 1532.

<sup>3</sup> R. Scholder and G. Sperka, *Z. anorg. Chem.*, 1956, **285**, 49.

<sup>4</sup> W. Klemm, *Angew. Chem.*, 1954, **66**, 468.

<sup>5</sup> N. Bailey and M. C. R. Symons, *J.*, 1957, 203.

<sup>6</sup> R. Scholder, *Angew. Chem.*, 1958, **70**, 583, and references therein.

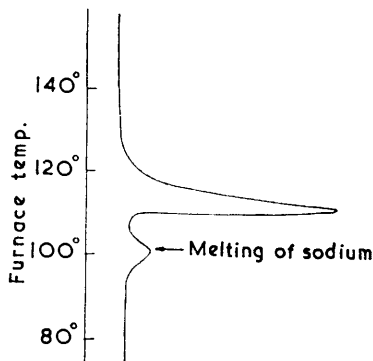
<sup>7</sup> H. L. Yakel, *Acta Cryst.*, 1955, **8**, 394.

<sup>8</sup> A. Wold and R. Ward, *J. Amer. Chem. Soc.*, 1954, **76**, 1029.

liquid sodium; no sodium oxide was produced, since the sodium surface remained bright throughout the reaction. Excess of sodium was distilled off at  $450^{\circ}/10^{-5}$  mm., when the product remained as a green powder. A typical differential-thermal-analysis trace (see Figure) illustrates the sudden nature of the reaction. With this oxide, it appears that the critical reaction temperature observed with many oxides cannot be observed, because it is below the melting point of sodium ( $98.6^{\circ}$ ), and reaction occurs only when the sodium has become molten. The quantities of sodium in the reaction and control vessels are not quite identical, so that melting is registered as a small peak on the trace. Thereafter, the wetting of the oxide before reaction requires a few minutes, so that the recorded reaction temperature varies somewhat with heating rate. At  $3^{\circ}$  per min., reaction occurred at  $108^{\circ}$ , but falls towards  $98.6^{\circ}$  at slower heating rates. There was no evidence of further reaction up to  $400^{\circ}$ .

*Analysis of Product.*—Protection from moist air was essential, the product being extremely deliquescent. On standing in the air, the product gave a yellow solution and a green residue

Differential thermal analysis of the liquid sodium-chromium trioxide reaction  
(0.07 g. oxide in 5 ml. liquid sodium:  
temperature rise on reaction,  $19^{\circ}$ )



within 2 min. It was necessary to determine sodium on solutions free from chromium; a stream of chlorine was therefore passed over a dry sample of the product at red heat in a porcelain boat, when the reaction



occurred. This reaction is strongly exothermic; on contact with chlorine, the product glows, but no sublimation occurs. All the chromium present was converted into chromium(III) oxide, which was identified by its *X*-ray powder pattern. The oxygen released in the reaction may be evolved as the element, or in the form of chlorine oxides. Sodium chloride was extracted with water, and the sodium determined in the solution with an Eel flame photometer. For chromium content, the product was converted into sodium chromate by fusion with potassium hydroxide (Found: Cr, 35.6; Na, 31.5. Calc. for  $\text{Na}_2\text{CrO}_3$ : Cr, 35.6; Na, 31.5%).

As a further test of the stability of the product, the reaction between liquid sodium and chromium trioxide was carried out at  $150^{\circ}$  in a nickel crucible as before, and the crucible and contents were then held at  $600^{\circ}$  for 12 hr. before the sodium was distilled off at  $450^{\circ}/10^{-5}$  mm. The product was chemically identical with that obtained at  $450^{\circ}$ .

*Density.*—This value was required in connection with the *X*-ray studies; it was determined using the method of Baker and Martin,<sup>9</sup> and involved the weight of the compound in argon and when immersed in carbon tetrachloride. Two samples each gave a density of  $3.847$  g./c.c. at  $20^{\circ}$ .

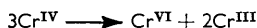
## RESULTS AND DISCUSSION

Values of the free energies of formation ( $-\Delta G_{298}$  per g.-atom O is  $40.3$  kcal. for  $\text{CrO}_3$  and  $84.4$  kcal. for  $\text{Cr}_2\text{O}_3$ ) indicate that chromium trioxide should be reduced by liquid sodium ( $-\Delta G_{298}$  for  $\text{Na}_2\text{O}$  is  $89.9$  kcal.), to an extent that will be determined also by the energy involved in ternary oxide formation. The high stability of the ternary oxide  $\text{Na}_2\text{CrO}_3$  clearly prevents reduction beyond the chromium(IV) stage.

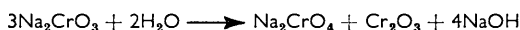
The compound has limited solubility in a lithium chloride-potassium chloride eutectic melt at  $375^{\circ}$ , giving a green solution in which the chromium(IV) oxidation state is presumably

<sup>9</sup> I. Baker and G. Martin, *Analyt. Chem.*, 1943, **15**, 279.

stable; on addition of a small quantity of molten potassium nitrate, oxidation to chromate(VI) occurred, and the colour changed immediately to yellow. When added to a lithium nitrate-potassium nitrate eutectic melt at 150°, the compound gave a yellow solution of chromate(VI) immediately. The green Cr<sup>IV</sup> species in the chloride melt was also unstable in the presence of traces of water, and when the melt was exposed to the atmosphere its colour changed to yellow within 15 min. When added to water, the compound disproportionates:



a yellow solution and a green precipitate were found to contain chromate and hydrated chromium(III) oxide in proportions required by the equation



*Magnetic Susceptibility.*—Measurements of the gram-susceptibility  $\chi_g$  at 24° gave values of  $17.68 \times 10^{-6}$  and  $18.21 \times 10^{-6}$  c.g.s. units for samples from two separate preparations, which correspond to  $\mu_{\text{eff}}$  values of 2.49 and 2.52 B.M. These are somewhat lower than the value of 2.82 B.M., which Klemm<sup>4</sup> has reported for Ba<sub>2</sub>Cr<sup>IV</sup>O<sub>4</sub>, and which is close to the spin-only value for two unpaired electrons in the Cr<sup>IV</sup> atom. We believe that the  $\mu_{\text{eff}}$  values are still consistent with the chromium(IV) oxidation state in Na<sub>2</sub>CrO<sub>3</sub>, in view of the higher chromium content in this compound and the greater possibility of metal-metal interaction.

*X-Ray Diffraction.*—This aspect was studied in order to establish the product as a single phase, but it was also of interest to determine the symmetry type, and the spatial arrangement of oxygen atoms around each chromium atom in a "metachromate" CrO<sub>3</sub><sup>n-</sup>. The diffraction patterns, obtained as already described,<sup>1</sup> are shown in the Table.

X-Ray diffraction patterns for Na<sub>2</sub>CrO<sub>3</sub>

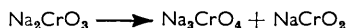
(a) Na-CrO<sub>3</sub> product heated at 450° for 16 hours

<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>1</sub>	<i>hkl</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>1</sub>	<i>hkl</i>	<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>1</sub>	<i>hkl</i>
5.367	70	006	1.710	10	20,14	1.335	5	40 $\bar{8}$
2.678	20	202	1.583	40	20,1 $\bar{6}$	1.302	10	20,2 $\bar{2}$
2.556	10	00,12	1.490	50	060	1.271	10	40,1 $\bar{0}$
2.466	30	20 $\bar{4}$	1.443	10	066	1.228	20	40,1 $\bar{6}$
2.172	100	208	1.361	5	00,24	1.179	20	

(b) Na-CrO<sub>3</sub> product heated at 600° for 12 hours

<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>1</sub>	<i>d</i> (Å)	<i>I</i> / <i>I</i> <sub>1</sub>
5.408	70	2.170	100	1.273	10
5.210	10	1.718	20	1.229	15
3.350	10	1.587	50	1.134	20
2.680	25	1.496	50	1.084	10
2.570	20	1.446	10	1.043	5
2.462	25	1.362	10	0.992	10
2.372	25	1.332	10	0.947	10
2.257	10	1.301	15	0.877	10

The diffraction pattern for the product formed at temperatures up to 450° was somewhat diffuse, and difficult to index. It could be indexed under two symmetry types: the first type involved<sup>5</sup> the tetragonal unit cell, with  $a = 6.504$  Å,  $c = 5.371$  Å, thus making the product isostructural with the compound Na<sub>2</sub>VO<sub>3</sub> prepared by Rudorff, Walter and Becker<sup>10</sup> for which unit cell dimensions  $a = 7.66$  KX,  $c = 5.31$  KX were quoted. However, the changes in the diffraction pattern that occur on prolonged heating at 600° (see Table) indicate that the tetragonal structure is unlikely; a sharper pattern is then obtained, and some line splittings become apparent. We have examined the possibility that this may be caused by the onset of the disproportion



<sup>10</sup> W. Rudorff, G. Walter, and H. Becker, *Z. anorg. Chem.*, 1956, **285**, 287.

which Scholder<sup>6</sup> considered might account for the absence of the compound  $\text{Na}_2\text{CrO}_3$  in his reaction products. The phase  $\alpha\text{-NaCrO}_2$  has the  $\alpha$ -sodium ferrate structure,<sup>11</sup> but the  $600^\circ$  pattern contains no lines which can be attributed to this  $\text{ABO}_2$  structure.

The line splitting which arises in the diffraction pattern on heating at  $600^\circ$  suggests strongly that the structure is, in fact, of a symmetry type lower than tetragonal. Lang<sup>12</sup> studied the compounds  $\text{Li}_2\text{SnO}_3$ ,  $\text{Li}_2\text{TiO}_3$ ,  $\text{Na}_2\text{SnO}_3$ ,  $\text{Na}_2\text{ZrO}_3$ , and  $\text{Na}_2\text{PbO}_3$ , and found them to be isotypical, with the monoclinic unit cell, with space group  $C2/c$  and eight formula weights per unit cell. Assuming that the product  $\text{Na}_2\text{CrO}_3$  has this structure also, approximate values for the monoclinic cell dimensions were obtained by comparison with the densities and cell dimensions of the compounds  $\text{Li}_2\text{TiO}_3$  and  $\text{Na}_2\text{ZrO}_3$ . These approximate values were then used to calculate corresponding values for  $\sin^2\theta_{hkl}$ ; these were sufficiently close to the actual values to confirm that the compound had monoclinic structure. Accurate values for the monoclinic lattice constants, obtained from the allocated  $hkl$  values and the experimental  $\sin^2\theta$  values, were  $a = 10.37 \text{ \AA}$ ,  $b = 8.81 \text{ \AA}$ ,  $c = 5.36 \text{ \AA}$ , and  $\beta = 99^\circ 48'$ . In this structure,<sup>12</sup> the  $\text{Cr}^{4+}$  ions are in 6-fold co-ordination with respect to oxygen.

Since there is no direct analogy between this structure and that of the parent  $\text{CrO}_3$ ,<sup>13</sup> the  $\text{Na}_2\text{CrO}_3$  structure is not formed simply by expansion of the  $\text{CrO}_3$  structure on penetration by sodium atoms. Such penetration is no doubt again the initial step in the reaction,<sup>1</sup> but complete regrouping of the atoms occurs on transfer of electrons from sodium atoms to chromium ions.

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<sup>11</sup> S. Goldsztaub, *Bull. Soc. franc. minéral.*, 1935, **58**, 6.

<sup>12</sup> G. Lang, *Z. anorg. Chem.*, 1954, **276**, 79.

<sup>13</sup> A. Bystrom and K. A. Wilhelm, *Acta Chem. Scand.*, 1950, **4**, 1131.

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