

NATURE OF THE REACTION PRODUCTS OF Na(l) WITH CrO<sub>3</sub>

H. van Lith, E.G. van den Broek \* and P.J. Gellings \*

\* Laboratory for Inorganic Chemistry and Materials Science,  
Department of Chemical Engineering, Technical University Twente,  
Postbox 217, Enschede, the Netherlands

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The X ray diffraction patterns of the compound existing in liquid sodium in the presence of chromium and oxygen, found by many investigators (1,2,3,4) and in our laboratory are identical. Most of the authors suggest this compound to be NaCrO<sub>2</sub>. Addison and Barker (1), however, suggest the formula Na<sub>2</sub>CrO<sub>3</sub> for this compound.

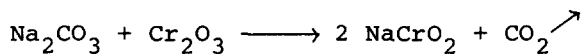
The patterns obtained by us, using CuK $\alpha$  radiation and a Debye-Scherrer camera of 114.7 mm diameter, are shown in the first two columns of Table 1.

TABLE 1  
Diffraction Patterns of NaCrO<sub>2</sub>

reaction Na(l)		solid state		Tech.Phys.Dienst		calculated	
d Å	I	d Å	I	d Å	I	d Å	I
5.27	60	5.33	100	5.32	70	5.31	90
2.64	8	2.657	40	2.662	20	2.66	20
2.54	4	2.540	40	2.542	20	2.54	6
2.447	10	2.449	40	2.451	40	2.446	30
2.152	100	2.161	100	2.164	100	2.160	100
1.697	4	1.707	40	1.707	10	1.704	10
1.567	20	1.575	70	1.578	20	1.575	20
1.485	30	1.487	70	1.487	40	1.484	30
1.405	2	1.433	40	1.432	20	1.429	8
1.356	4	1.335	40	1.357	6	1.355	10
-	-	1.328	40	1.331	2	1.328	2
1.303	6	1.298	40	1.298	8	1.296	10
-	-	-	-	1.271	6	1.269	4
-	-	1.264	20	1.265	2	1.262	4
1.235	6	1.224	40	1.226	8	1.223	10

In the first column of Table 1 the pattern of the product obtained from the reaction of CrO<sub>3</sub> with an excess of liquid sodium is given. The sodium is saturated with oxygen at the reaction temperature, being 320 °C. The reaction time was 14 days. Before analysing the product, the sodium is distilled off (400 °C, 10<sup>-2</sup> mm Hg during 10 hours).

The pattern in the second column has been obtained on the product of the solid state reaction by Van Leuven (3):



(powdered mixture heated at 900 °C in an argon atmosphere during two hours).

The pattern in the third column has been obtained by the Tech. Phys.Dienst (4) on a product prepared by the same solid state reaction.

The pattern shown in the last column has been calculated using the structural data, shown in Table 2, proposed by Rüdorff and Becker (5) as mentioned by Wyckoff (6). Comparison of the different columns of Table 1 shows the agreement between the experimental and the calculated patterns.

TABLE 2

The Hexagonal Unit Cell of NaCrO<sub>2</sub>. Space group R $\bar{3}m$  - D<sub>3d</sub><sup>5</sup>

Na	(0,0,0)	}	
Cr	(0,0, $\frac{1}{2}$ )		+ (0,0,0)
O <sub>I</sub>	(0,0,u)		+ (1/3,1/3,1/3)
O <sub>II</sub>	(0,0, $\bar{u}$ )		+ (2/3,1/3,1/3)
a = 2.968 Å ; c = 15.94 Å ; u = 0.22			

Calculating the value of "u" using the patterns found by Addison et.al. (1), Gross et.al. (2), Van Leuven (3), the Tech. Phys.Dienst (4) and in our laboratory with a least squares refinement program by Rietveld (7) yields  $u = 0.220 \pm 0.015$ ; in these calculations the Na<sup>+</sup> ion has the (0,0,0) position. This, therefore, also confirms the results obtained by Rüdorff et.al.

Because the diffraction pattern found by Addison et.al. (1) as mentioned by the A.S.T.M. Powder data file (8) agrees with other investigators (2,3,4) as well as with the patterns

observed and calculated by us, this shows that it is highly improbable that the formation of his product as Na<sub>2</sub>CrO<sub>3</sub> having the Li<sub>2</sub>SnO<sub>3</sub> structure is correct.

#### ACKNOWLEDGEMENT

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