

## Note on the Crystal Structure of Ferromagnetic Chromium Dioxide

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The formula  $\text{CrO}_2$  for the ferromagnetic chromium oxide was established by Michel and Bénard in 1935<sup>1,2</sup>. They found that this phase is of a rutile type. The compound has subsequently been studied by several investigators<sup>3-6</sup>.

The following methods have been used for preparing chromium dioxide:

- thermal decomposition of  $\text{CrO}_2\text{Cl}_2$ <sup>1,3,5</sup>
- thermal decomposition of pure  $\text{CrO}_3$  under oxygen pressure<sup>3,4</sup>
- thermal decomposition of aqueous  $\text{CrO}_3$ -solution under oxygen pressure<sup>6</sup>

Method A) seems to give a product which is contaminated with  $\text{Cr}_2\text{O}_3$  and method B) a product contaminated with higher chromium oxides<sup>3</sup> or  $\text{Cr}_2\text{O}_3$ <sup>3,4</sup>. In Ref.<sup>6</sup> the product (method C) is characterized as "X-ray pure" but no analytical data are given.

Bhatnagar<sup>7</sup> has reported a normal paramagnetic susceptibility corresponding to two unpaired electrons per Cr atom for a substance said to be  $\text{CrO}_2$ . On the other hand, the ferromagnetism of  $\text{CrO}_2$  has been recently confirmed by Glemser<sup>5</sup> and by Ariya *et al.*<sup>4</sup>

This paper gives the results of an X-ray diffraction study of an oxide sample obtained by thermal decomposition of pure  $\text{CrO}_3$  (Baker's analyzed, dried over  $\text{P}_2\text{O}_5$ ) at 350°C under oxygen pressure (60 atm). The material so obtained consisted of opaque, black, strongly magnetic crystalline aggregates. The sample was dissolved in hot concentrated sulphuric acid and the chromium content determined using Mohr's salt and standard permanganate solution after oxidation by peroxodisulphate in the presence of silver ions. The composition of the sample was found to be  $\text{CrO}_{2.14}$ .

Table 1 lists results reported by previous authors and those obtained in this investigation. The unit cell dimensions of the rutile-type structure were in all cases derived from X-ray powder patterns. Our data were obtained from a Guinier powder photograph taken with  $\text{CuK}\alpha_1$  radiation

Table 1.

Reference	Mean composition of sample	a Å	c Å	Density
2	$\text{CrO}_{1.8}$	4.41	2.86	—
3	—	4.43 *	2.92 *	—
4	$\text{CrO}_{1.98}$	4.394	5.77	4.90
5	$\text{CrO}_{1.9}$	4.41	2.91	4.80
6	—	4.421	2.916	—
This investigation	$\text{CrO}_{2.14}$	4.423	2.917	4.83

\* Calculated from the *d*-values given in Ref.<sup>3</sup>

using potassium chloride ( $a = 6.2919$  Å) as an internal standard (*cf.* Table 2). The back-ground fogging caused by the fluorescence radiation from chromium was effectively depressed by means of an aluminium foil (35  $\mu$ ) covering the photographic film. Even in amply exposed photographs it was not possible to find indications of a doubling of the *c* axis as

Table 2. X-Ray powder pattern of a sample with the mean composition  $\text{CrO}_{2.14}$

<i>hkl</i>	<i>I</i> <sub>obs</sub>	$\sin^2\theta_{\text{obs}}$	$\sin^2\theta_{\text{calc}}$
—	w *	0.05568	—
110	v st	0.06066	0.06067
101	v st	0.10002	0.10003
200	v w	0.12133	0.12137
111	m	0.13036	0.13038
210	v w	0.15166	0.15167
211	v st	0.22135	0.22137
220	m	0.24266	0.24255
002	w	0.27876	0.27869
310	w	0.30332	0.30330
102	—	—	0.30910
221	—	—	0.31235
112	w	0.33943	0.33931
301	w	0.34268	0.34269
311	—	—	0.37301
320	—	—	0.39432
202	—	—	0.40009
212	—	—	0.43042
321	v w	0.46401	0.46399

\* The presence of this line suggests that the excess oxygen content of the sample over the composition  $\text{CrO}_2$  is due to a contamination by the phase  $\text{CrO}_{2.5}$ , the strongest reflexion of which occurs at  $\sin^2\theta = 0.0558$  as calculated from the data given by Schwartz *et al.*<sup>3</sup>

reported by Ariya *et al.*<sup>4</sup> The observed density is in good agreement with the value of 4.89 g/cm<sup>3</sup> calculated for a cell content of two formula units of CrO<sub>2</sub>.

The axial ratio of chromium dioxide ( $c/a = 0.660$ ) corresponds to a relatively long distance between adjacent Cr atoms and indicates that no attracting forces are acting between these metal atoms in contrast to what is the case in several other compounds of transition metals with valency states lower than their maximum ones<sup>5</sup>. Of particular interest in this connection is the rutile type phase (Cr, Mo)O<sub>2</sub> with its considerably lower values of  $c/a$  (down to 0.60) which have been interpreted as caused by the presence of metalmetal bonding<sup>6</sup>.

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## Chemical Synthesis of Oleyl Adenylate

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Mixed anhydrides of adenylic acid with short and middle chain fatty acids have been proposed as intermediates in the

enzymatic activation of these acids to their CoA derivatives<sup>1-5</sup>. Chemical synthesis of these adenylates has been reported using three different methods: 1) coupling of silver adenylate with the acid chloride (acetyl adenylate<sup>1</sup>), 2) the reaction of the acid anhydride with adenylic acid in aqueous pyridine (buturyl and hexanoyl adenylate<sup>2,5</sup>), and 3) the condensation of fatty acid and adenylic acid in the presence of carbodiimides (buturyl adenylate<sup>5</sup>).

For an attempted synthesis of long chain fatty acid adenylates method 2 did not seem practical due to the low solubility of the long chain anhydrides. Of the two other methods the carbodiimide method was found to be the most practical and to give the best yields.

This paper will describe the synthesis of oleyl adenylate by the condensation of oleic acid with adenylic acid in the presence of dicyclohexylcarbodiimide and also includes experiments to show the metabolic activity of this compound with rat liver mitochondria *in vitro*.

## EXPERIMENTAL

**Materials.** Adenylic acid (AMP) was obtained from Sigma Chemical Company and dicyclohexylcarbodiimide (DCC) from Fluka A.G.

**Methods.** Oleyl adenylate was estimated by the hydroxamic acid-FeCl<sub>3</sub> method modified for the acid insoluble hydroxamates of oleic acid<sup>6</sup>. A sample containing approximately 1 mg adenylate in 0.1—0.5 ml was added with 1 ml of a freshly prepared solution of equal volumes of 28% hydroxylamine and 14% sodium hydroxide. After 5 min 3 ml of 7% perchloric acid was added and the insoluble hydroxamates filtered off on a paper filter (Munktell No. 8, diam. 5.5 cm) and washed on the filter two times with each 3 ml of the perchloric acid solution. The hydroxamates were then extracted from the filter with 3 ml of a dilution of Hill's reagent 1:20 in ethanol and the extinction of the solution measured at 530 m $\mu$ . With this method 1  $\mu$ mole hydroxamate gives an extinction of 0.28, the molecular extinction of hydroxamates being around 1 000.

**Synthesis of oleyl adenylate.** 1 g adenylic acid (= 2.74 mmole) was dissolved in 40 ml pyridine and 8 ml water and 10 ml oleic acid (= 30 mmole) added. This solution was cooled to 0° and was added to an ice-cold solution of 10 g DCC in 20 ml pyridine. The reaction mixture was allowed to stand for 6 h in an ice-bath and was then added with 32 ml ice-cold