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Hexagonal High Temperature Polymorph of Calcium Chromite^{1a}

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Calcium chromite exists in two polymorphic forms. The low temperature modification, β -CaCr₂O₄, is isostructural with CaFe₂O₄ and CaV₂O₄.²⁻⁴ The high temperature form, stable above 1570°,⁵ was designated α -CaCr₂O₄ by Ford, *et al.*⁶ A powder pattern was reported and a tetragonal unit cell with $a = 5.53 \text{ \AA}$, $c = 19.16 \text{ \AA}$ deduced from it. A single crystal study conducted in this Laboratory indicates that the unit cell is hexagonal.

Experimental

Reagent grade CaCO₃ and Cr₂O₃ were dried at 350° and 1000°, respectively. The equimolar composition was weighed out, ground under alcohol in a mortar, and air dried. This intimate mechanical mixture was compressed into small pellets using a hand press. Pellets heated in air (24 hr., 1350°), gave an X-ray powder pattern of β -CaCr₂O₄. These pellets, and also unreacted pellets of the CaCO₃ + Cr₂O₃ mixture, were heated in a gas-oxygen flame. The hottest portions of the pellets were converted to α -CaCr₂O₄. The X-ray powder pattern (Table I) was nearly identical with that obtained by Ford, *et al.*⁶ No difficulty was experienced in quenching the α -CaCr₂O₄ to room temperature.

α -CaCr₂O₄ is very refractory. Although a small piece of platinum foil placed over the top and side of a pellet prior to heating was thoroughly melted, the pellet itself showed no signs of melting. Consequently, the crystals produced in a gas-oxygen flame were too small for single crystal work.

The pellets could be melted in an oxyhydrogen flame; the tip of a pellet was melted, and allowed to freeze by gradually withdrawing the flame. Single crystals selected from the crushed tip using a petrographic microscope gave rotation photographs matching the powder photographs of α -CaCr₂O₄.

Chromium oxide is known to be volatile at high temperatures. In order to check the possible loss of chromium

TABLE I
POWDER DATA FOR α -CaCr₂O₄

I^a	d (Å.)		hkl
	obsd. ^a	(calcd.)	
m	5.56	5.54	00.2
w	3.60	3.61	21.1
vwv	(3.14)	3.14	21.2
w	2.77	2.77	00.4
vw	2.65	2.65	21.3
mw	2.52	2.53	40.0
ms	2.31	2.30	40.2
m	2.085	2.085	40.3
s	1.865	1.866	40.4
m	1.490	1.490	40.6
m	1.459	1.459	44.0
vw	(1.414)	1.411	44.2
w	1.388	1.382	00.8
w	1.290	1.290	44.4
vwv	(1.232)	1.232	80.2
mw	1.215	1.215	40.8
vwv	(1.197)	1.195	80.3
w	(1.152)	1.149	80.4

^a Filtered CuK α radiation: 36 kv., 15 ma. Observed d spacings obtained from diffractometer traces using a Phillips Type PW 1051 machine at a scanning speed of $1/2^\circ$ 2 θ per min.; except those marked () which were obtained from 6-cm. films. Diffractometer results were corrected from an external silicon standard; film results are uncorrected. The intensities were estimated visually from a film, on a scale ranging from the strongest (s) through progressively weaker (ms, m, mw, w, and vw) to the weakest visible (vwv).

oxide, a number of crystal fragments were hand picked under the microscope, sealed into an evacuated silica tube, and heated at 1350° for 24 hr. The sample was converted into β -CaCr₂O₄ with no other phases present, judging by the X-ray powder pattern. Thus the fusion does not change the Ca:Cr:O ratio of the sample, within the limits of the method (~5% of an extraneous phase).

Results and Discussion

Rotation and Weissenberg photographs about a and c , and a Laue photograph taken with the beam directed parallel to c , showed that the crystals were hexagonal with $a = 11.67 \pm 0.01 \text{ \AA}$, $c = 11.07 \pm 0.01 \text{ \AA}$. The powder pattern was indexed on the basis of this cell (Table I), assigning indices to lines by direct comparison of the c -rotation photograph with a powder pattern taken on the same camera.

It is very noticeable that reflections for which $h = 4n$ and $l = 2n$ are much stronger than the others, giving a hexagonal pseudo-cell, 1/32 the volume of the true cell, with $a = 2.92$, $c = 5.53$. Inspection of the powder pattern (Table I) shows that most of the lines will index on this cell, those which will not being mostly weak or very weak lines at low angles.

(1) (a) This research has been supported by the Air Force Office of Scientific Research of the Air Research and Development Command, United States Air Force, through its European Office; (b) Department of Chemistry, University of Aberdeen, Scotland.

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Because of this systematic weakness, it is very difficult to decide what, if any, are the systematic absences of the true cell. Indices of the type $hh2\bar{h}l$ appear to be absent for l odd and this, if it is a true absence, fixes the space group as $P6_3mc$, $P6_2c$, or $P6_3mmc$.

Because of the method of preparation of the sample, the quantity available was too small to attempt a density determination by a bulk method, and sufficiently dense liquids were not available to attempt a sink-or-float determination. Ford, *et al.*,⁶ give $d = 4.70$; using this value $Z = 17.8$ (or 18) for the true unit cell. $Z = 18$ is compatible with any of the possible space groups.

The lines in the α - CaCr_2O_4 powder pattern index equally well on the tetragonal cell proposed by Ford, *et al.*,⁶ or on the true hexagonal cell. Unit cells deduced from powder data alone are not reliable except in very simple cases.

The value of the a axis of the pseudo-cell (~ 2.9 Å.) suggests that the structure contains sheets of approximately close-packed oxygen atoms perpendicular to c . The pseudo-cell then would contain one oxygen of each layer, and the true cell sixteen, affording a plausible explanation of the systematic weakness. From the length of the c -axis, it also is apparent that the layers are not entirely close packed in the c -direction. The number of atoms in the true cell is too great for any attempt to be made at guessing a structure. It seems likely, however, that α - CaCr_2O_4 represents a new hexagonal structure type unrelated either to the stuffed-silica-like BaAl_2O_4 or to the spinel structure.

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Vapor Phase Pyrolysis of the Lower Alkyl Orthoborates

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The thermal decomposition of the higher alkyl orthoborates has received some attention. Thus, tri- n -hexyl, n -octyl, n -decyl,¹ n -dodecyl,² and 1-

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menthyl³ orthoborates have been shown to give the corresponding olefins in good yield. By contrast, virtually no information is available on the pyrolysis of the lower esters. Makishima, Yoneda, and Tajima⁴ found trimethyl orthoborate vapor stable up to 470° , the highest temperature attainable with their Pyrex glass apparatus. Washburn, *et al.*,⁵ observed very slight decomposition on refluxing tri- n -butyl orthoborate for one hour at atmospheric pressure (b.p. 230.0 – 231.0^{06}), but did not analyze the products.

We have made a preliminary study of the vapor phase pyrolysis of the methyl, ethyl, n -propyl, isopropyl, and n -butyl esters, with emphasis on the temperature of decomposition and the identity of the products. The results are summarized in Tables I and II, in which are listed the temperature range of each experiment and the composition of the volatile products at various times during the decompositions. Some trace components are not included. The lower temperature quoted for each ester is the temperature at which decomposition first became measurable. The pyrolyses of methyl and ethyl borates were carried almost to completion and the solid residues found to consist of hydrated diboron trioxide plus, in the case of methyl borate, a material which might be an organic polymer.

Of the esters studied, only isopropyl borate decomposed cleanly, giving substantially pure propylene at the beginning of the pyrolysis.

Experimental

General Procedure.—The esters, supplied by the U.S. Borax and Chemical Corp., Pacific Coast Borax Company

TABLE I
PRODUCT COMPOSITION IN MOLE %

R in B(OR) ₃ Decomn. temp., °C.	CH ₃ 530–555			C ₂ H ₅ 415–460		
	1	4.5	10.5	2	10	11
Reaction time, hr.						
H ₂	48.4	58.5	80	16.9	20.3	18.9
CO	28.0	29.8	16	2.8	21.4	22.0
CH ₄	23.6	11.7	4	4.4	25.4	25.7
C ₂ H ₄				73.8	23.9	19.4
C ₂ H ₆				2.1	9.0	12.5

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