octahedron.[15] The broad band at 540 cm.$^{-1}$ can therefore be considered the ν_3 frequency arising from an octahedral species of O_h symmetry and is comparable to the value of 511 cm.$^{-1}$ observed[16] for K_3VF_6. The suggestion was made previously[2] that vanadium tetrafluoride has an associated structure in which four fluorine atoms of each VF_6 octahedral unit are shared with adjacent octahedra. The symmetry about the vanadium is therefore probably tetragonal rather than octahedral. A molecule of tetragonal (D_{4h}) symmetry has three infrared active fundamentals (doubly degenerate E_u species) rather than the two triply degenerate infrared active fundamentals of an octahedral molecule. Assuming that small changes in symmetry such as this will not cause large shifts in the vibrational frequencies, the 780–837 cm.$^{-1}$ band in vanadium tetrafluoride may be considered one of these three fundamentals. The strong band at 540 cm.$^{-1}$ probably corresponds to the 583 cm.$^{-1}$ band observed in K_2VF_6,[16] and the remaining fundamental may be below 400 cm.$^{-1}$. The reason for the doublet structure of the 780–837 cm.$^{-1}$ peak is not clear, but it may be due to crystal field effects or to differences in bonding.

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CONTRIBUTION FROM THE SPERRY RAND
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A New Polymorph of CrOOH

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Compounds in the system chromium–oxygen–hydrogen have been of interest in regard to magnetic properties,[1] catalytic action,[2] and pigment applications.[3] The chemistry of the system is complex, in view of the multivalence of chromium, and experimental work is hindered by the occurrence of poorly crystallized products. The present work involved reactions under hydrothermal conditions, using sealed platinum tubes inside Stellite pressure vessels,[4] and has yielded additional information concerning the solid phases and their interconversion. The use of hydrothermal reaction conditions is favorable in this type of system, both in order to promote crystallization and to permit retention of the higher valence states of chromium. Previous investigations[5–8] have shown that, in addition to CrO_3 and Cr_2O_3, the compounds CrO_2 and CrOOH (I) can occur. Various hydrated oxides, usually poorly crystallized and of uncertain composition, have been described, and also a metastable "cubic γ-Cr_2O_3," analogous to γ-Fe_2O_3.[5] The crystal lattice of the CrOOH compound (I) was deduced as rhombohedral by Thamer, Douglass, and Staritzky.[7] Their material was obtained as brown-red crystals by decomposition of CrO_3 in water under hydrothermal conditions. They also observed coexistence of CrO_2 in some experiments, but the conditions favoring formation of either product were not defined. Laubengayer and McCune[5] treated a precipitated hydrated chromium oxide in water or aqueous NaOH solution, at high temperature and pressure, and obtained a blue-gray compound (II). The chromium content of II was consistent with CrOOH, and the compound gave the same X-ray pattern as that subsequently reported for I. In the present work, treatment of CrO_3, either in the presence of water or nominally in the dry state, at 450° under a total pressure of 40,000 p.s.i., has yielded the black, magnetic CrO_2. This result is consistent with earlier reports.[8–12] Substitution of 0.25 M $K_2Cr_2O_7$ solution for water in two experiments yielded the red CrOOH (I), although this has not been established as a consistent result. Treatment of CrO_2, obtained as described above, in water at 450° and 40,000 p.s.i., yielded a green product (III), which gave an X-ray pattern distinct from those of the known phases in this system. Emission spectrographic examination showed only chromium as a major constituent. Gravimetric determinations were consistent with the empirical formula CrOOH for III. The crystal lattice of III has been determined as orthorhombic, with a = 4.861, b = 4.292, c = 2.960 Å.

Experimental

The compound CrO_2 was prepared by decomposition of CrO_3, by heating for 72 hr. at 450° and 40,000 p.s.i., using welded thin-walled platinum tubing as a reaction container. The pressure and temperature were provided by means of a Stellite pressure vessel heated in a tube furnace, according to conventional techniques. The CrO_2 was removed from the reaction tube, washed in water, and ~0.2 g. was resealed in a new platinum tube, together with ~2 ml. of water. The CrO_2–water mixture was then heated for 72 hr. at 450° and 40,000 p.s.i. The reaction product was an olive-green powder (III) which gave the X-ray diffraction powder data shown in Table I.

X-Ray diffraction powder patterns were obtained using a 114.59-mm. Straumanis-loaded camera, with vanadium-filtered chromium radiation. Intensity measurements were made by visual estimation.

The powder pattern was indexed on an orthorhombic cell with a = 4.861, b = 4.292, and c = 2.960 Å. The indexing was done

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TABLE I
X-RAY DATA FOR CrOOH (III)

Orthorhombic indices *hkl*	*I* obsd.	*d* obsd., Å.	*d* calcd., Å.
110	s	3.214	3.217
101	m−	2.522	2.528
011	m+	2.429	2.437
200			2.431
111	m−	2.174	2.178
020	w−	2.145	2.146
210	m−	2.112	2.115
211	m	1.720	1.721
121	m+	1.636	1.636
220	m−	1.608	1.609
310	w	1.515	1.516
002	w	1.478	1.480
301	m−	1.421	1.421
130	w	1.373	1.372
112	m−	1.343	1.345
031	w	1.288	1.288
202	w	1.263	1.264
131	w	1.245	1.245
230	w	1.233	1.233
212	w	1.212	1.213
400			1.215
122	w	1.185	1.182
321			1.185

by examining differences of $\sin^2 \theta$ values. The unit cell was corroborated by electron diffraction data.

An approximate mean refractive index of 1.9 was determined microscopically by the immersion method. The material was light yellow-green in transmission, but was too finely divided for any individual crystal to be distinguished. Individual crystals as observed in the electron microscope had no recognizable outline, although they were shown to be single by selected area electron diffraction.

An identical product III was obtained by similar treatment of CrO_2 in 3 *M* NaOH or 0.25 *M* $K_2Cr_2O_7$ solutions, instead of water.

Heating of III at 110° in air caused no loss in weight. Ignition at 1000° yielded Cr_2O_3, with a weight loss of 11.05%. No foreign lines were detected in the X-ray powder diffraction pattern of the Cr_2O_3, using Cr Kα radiation. The weight loss was shown to represent H_2O by direct collection and weighing. A weighed sample of III was sealed in an evacuated fused silica tube fitted with a small-bore side arm. The side arm was cooled with Dry Ice, and the sample was heated to red heat with a hydrogen torch. Water was seen to condense in the side arm and was ultimately caused to accumulate at the end of the side arm, which was then sealed off and separated from the main tube. The tube containing the collected water was allowed to reach room temperature, and a small opening was made by breaking off the pointed end of the glass. The tube was immediately weighed. It was then heated at 110° and reweighed. The weight loss corresponding to the collected water was 11.11% of the sample weight. The weight loss calculated for the reaction $2CrOOH \rightarrow Cr_2O_3 + H_2O$ is 10.59%. The empirical formula of III is therefore assumed to be CrOOH.

Samples of I and III were placed in unsealed envelopes of platinum foil and heated simultaneously at 335° in air in a tube furnace. After 6 hr., X-ray diffraction showed that III had converted completely to CrO_2, whereas I showed only partial conversion. After a further 72 hr., III still yielded only CrO_2, but I gave a mixture of CrO_2 and Cr_2O_3. More prolonged heating, for a total of 225 hr. at 335°, produced no further change in either sample.

Discussion

Treatment of CrO_2 in water at temperatures near 450° yields a green compound of empirical formula CrOOH. This appears to be a new phase modification of CrOOH, of orthorhombic structure, in contrast to the previously reported red, rhombohedral form. Direct interconversion of the two forms has not been observed. Heating of the green, orthorhombic form in air at about 350° causes complete and ready conversion to CrO_2, which is stable under these conditions. Similar heating of the red, rhombohedral form causes a slower conversion to CrO_2, mixed with some Cr_2O_3. The Cr_2O_3 content does not increase once all the CrOOH has been decomposed. This difference in behavior may be explained by the physical form of the green, orthorhombic CrOOH, which was much more finely divided and would be expected to oxidize more readily during decomposition, thereby avoiding the formation of unreactive aggregates of Cr_2O_3. Somewhat similar behavior is also found in the oxides and oxyhydroxides of iron. The following reversible reaction has thus been demonstrated for the green, orthorhombic CrOOH

$$2CrO_2 + H_2O \underset{350^\circ \text{ in air}}{\overset{450^\circ \text{ under pressure}}{\rightleftarrows}} 2CrOOH + (1/2)O_2 \qquad (1)$$

This reaction appears to be the first reported route to synthesis of pure CrO_2 under atmospheric conditions,[1] although it is necessary to use hydrothermal conditions to prepare the intermediate green, orthorhombic CrOOH.

Formation of the red, rhombohedral CrOOH has been considered[7] in terms of a reaction between protons and polymeric Cr^{VI} ions $(HCrO_4)_n^{-n}$

$$nH^+ + (HCrO_4)_n^{-n} = nCrOOH + (3n/4)O_2 + (n/2)H_2O \qquad (2)$$

In contrast, the green, orthorhombic CrOOH now reported appears to result from direct hydrolysis of CrO_2, according to eq. 1.

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Samarium and Lanthanum Tungstates of the $3R_2O_3 \cdot WO_3$ Type

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In the course of a recent investigation, four stable phases were found along the Sm_2O_3–WO_3 join[1] in the system Sm–W–O. The Sm_2O_3:WO_3 ratios for these phases are 1:3, 1:1, 7:4, and 3:1. Among the five

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