

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

New Crystalline Phases in the System Chromium(III) Oxide-Water¹BY A. W. LAUBENGAYER AND H. W. McCUNE²

The system chromium(III) oxide-water has been studied by the hydrothermal method in the temperature range 145–560°. The phases formed were characterized by the powder X-ray diffraction method, differential thermal analysis and chemical analysis. A definite compound, blue-gray CrOOH, having a density of 4.12 g./cc., is formed in the hydrothermal bomb below 419–424°. Differential thermal analysis showed that it decomposes sharply and endothermically at about 430°. By using a dilute solution of sodium hydroxide in the bomb instead of water, the rate of formation of CrOOH is greatly increased. Rhombohedral dichromium trioxide is the stable phase above 450°. The possibility that a CrOOH-dichromium trioxide transition exists at 419–424° is discussed. The existence of a cubic chromium oxide isomorphous with γ -Fe₂O₃ or Fe₃O₄ is indicated by the evidence presented.

Introduction

The work of several investigators has shown that in addition to the well known rhombohedral dichromium trioxide there are probably two other chromium compounds in the systems chromium(III) oxide-water. The blue-green hydrous oxide, although usually amorphous and of indefinite composition, appears to contain crystalline Cr(OH)₃ when prepared under certain conditions.^{3,4} At elevated temperatures and pressures, a compound having the composition CrOOH has been reported to be formed.^{5,6} Our investigation was undertaken to provide a survey of phases formed from hydrous chromium(III) oxide by the already well proven hydrothermal method⁷—thus avoiding in part difficulties due to the sluggish transitions characteristic of hydrous oxides.

Experimental

Experimental Techniques.—Details of the hydrothermal apparatus and procedure have been reported in earlier papers.⁸ Briefly, a platinum crucible was filled with the substance to be investigated, covered with platinum foil, and placed in a strong stainless steel bomb with water or an aqueous solution of sodium hydroxide. The bomb, after being held at a constant temperature for the desired time, was quenched to freeze the equilibrium. The degree of filling, in every case 0.7, determined the pressure in experiments above the critical temperature of water. Before sealing the bomb, air was flushed from the remaining space with nitrogen. A bridge controlled thyatron thermostat regulated the temperature of one furnace to $\pm 0.5^\circ$; a second furnace having no controller was used in experiments not requiring maintenance of a constant temperature. Considering possible sources of error, the temperature of the contents of a bomb probably could be measured by means of a thermocouple in the wall to $\pm 2^\circ$.

Starting materials and all products of hydrothermal experiments were examined by the powder method of X-ray diffraction, using a Norelco unit. MoK α -radiation was usually employed, but some exposures made with CrK α -radiation improved the values of the longer spacings. After drying in air at 105–110°, the products were analyzed by ignition to dichromium trioxide under hydrogen at 800 to 850°. Powder photographs verified the identity of the ignited product and this method of analysis was further checked by determining the chromium content of several

samples by titration. Fusion with sodium peroxide made possible solution of hydrothermal products for these analyses. Differential thermal analyses, in an apparatus similar to that described by Speil, *et al.*,⁹ were used to further characterize starting materials and products.

Preparation and Characterization of Hydrous Chromium(III) Oxide.—The starting material for most experiments was prepared by adding a slight excess of ammonia to a 0.1 M solution of chromium(III) chloride. Repeated washings by centrifugation and decantation removed the chloride from the resulting precipitate. As other workers have noted^{3,4} such a preparation gave several slightly broadened X-ray diffraction lines. A preparation made in a similar way from nitrate solution showed the same lines and several additional lines corresponding to shorter interplanar spacings. The X-ray diffraction data for such a preparation tabulated in Table II are in essential agreement with those obtained by Milligan from a preparation identified as Cr(OH)₃ with additional adsorbed water.^{4,10}

A differential thermal analysis curve of hydrous chromium oxide dried at 25° in a vacuum for 12 hours is shown in Fig. 1a. The initial valley was caused by the absorption of heat during dehydration, while the sharp exothermic peak at about 420° was associated with a sudden decrease in surface and crystallization of dichromium trioxide. This sudden liberation of heat, sometimes called the "glow phenomenon," has been investigated by Wöhler.¹¹

Hydrothermal Experiments in Water.—Hydrous oxide precipitated from chloride solution was used as starting material for a temperature survey of the phases formed in the hydrothermal bomb (Table I). All products prepared at 419° or below contained less than 61.2% chromium, which is the theoretical percentage in CrOOH; as the temperatures approached 419° the composition of the products approached the theoretical value and the color changed from the blue-green of the starting material to a blue-grey. X-Ray powder diffraction photographs of the products developed from a few diffuse bands for products prepared at lower temperatures to a series of almost sharp lines. Microphotometer tracings of those too diffuse to measure showed that the diffraction bands had peaks in the same positions as the sharper lines. The spacings calculated from this pattern were assigned to CrOOH and are listed in Table II. The conversion of amorphous hydrous oxide to crystalline CrOOH could also be followed by differential thermal analyses of the products. For example, Fig. 1b for product 19 shows a gradual absorption of heat, associated with dehydration of the hydrous oxide, superimposed on the endothermic decomposition of the CrOOH present in the sample. Curve c shows the sharp endothermic decomposition of CrOOH.

Products of runs made above 419° gave new X-ray diffraction lines and contained more than 61.2% chromium. Exceptions are products 7 and 8 which were held at temperature for only short times. Products prepared at temperatures above 450° were identified by X-ray diffraction as the common rhombohedral dichromium trioxide. X-Ray diffraction pictures of products made between 419 and 450° gave spacings, in addition to those of CrOOH, which were similar to those of γ -Fe₂O₃ or Fe₃O₄. The possibility that these spacings originated in an iron oxide contaminant from the bomb was discarded, since analysis showed that the

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TABLE I
PHASES FORMED FROM HYDROUS CHROMIUM(III) OXIDE IN
THE HYDROTHERMAL BOMB

Expt.	Temp., °C.	Time, hours	Cr, %	Product X-ray patterns	
1	550-570	50	..	Cr ₂ O ₃	
2	460-480	92	62.5	Cr ₂ O ₃	CrOOH ^a
3	450	195	68.4	Cr ₂ O ₃	CrOOH ^a
4	440-460	92	..	cu. oxide	CrOOH
5	448	165	..	cu. oxide	CrOOH
6	443	195	64.5	cu. oxide	CrOOH
7	438	40	60.6		CrOOH
8	433	42	60.5		CrOOH
9	424	260	65.4	cu. oxide	CrOOH
10	419	352	60.8		CrOOH
11	414	40	59.6		CrOOH
12	410	90	59.7		CrOOH
13	395-414	20	54.8		CrOOH ^b
14	365-400	74	59.1		CrOOH ^b
15	365-390	72	58.5		CrOOH ^b
16	360-380	168	..		CrOOH
17	314	165	59.2		CrOOH
18	250-300	93	56.5		CrOOH ^b
19	223-243	174	55.3		CrOOH ^b
20	135-155	330	53.0		CrOOH ^b

^a The appearance of 1 to 4 of the most intense lines of the characteristic pattern indicated the presence of a small amount of this compound. ^b These samples gave quite diffuse CrOOH patterns.

TABLE II
X-RAY POWDER DIFFRACTION DATA
vs = very strong, s = strong, m = medium, w = weak,
vw = very weak

Hyd. oxide		CrOOH		Cubic oxide	
d/n, Å.	Int.	d/n, Å.	Int.	d/n, Å.	Int.
4.9-4.5	vs	4.46	vs	2.95	w
3.38	vs	2.42	vs	2.52	vs
2.90	m	1.85	s	2.09	w
2.34	m	1.49	m	1.707	vw
2.19	w	1.41	m	1.610	w
2.10	w	1.28	vw	1.478	m
1.78	m	1.18	vw	1.277	vw
1.64	w	1.11	vw	1.088	vw
1.53	vw	1.06	w	0.8075	vw
1.46	vw	0.965	w		
1.39	vw	.890	vw		
1.32	vw	.856	vw		
1.29	vw	.842	vw		
1.22	vw	.744	vw		
1.17	vw				
1.11	vw				
1.02	vw				
0.989	vw				

samples contained less than 0.4% iron as Fe₂O₃ whereas the intensities of the new lines relative to those of CrOOH showed that the bulk of the material gave the new pattern. Interplanar spacings for this material are listed in Table II under "cubic oxide" since the similarity to the cubic iron oxide patterns indicates that this is a chromium isomorph.

A unit cell of 8.36 ± 0.02 Å. was calculated from the spacings obtained from the cubic chromium oxide. Unfortunately, all products which gave this cubic pattern also contained CrOOH so that the formula of the new compound could not be determined by analysis. Ignition (850°) in air converted the brown cubic oxide quickly to the common rhombohedral Cr₂O₃; the change occurred less rapidly in hydrogen. If the cubic chromium oxide were monotropic, as is gamma Fe₂O₃, its transition to the stable form should be exothermic. A differential thermal curve (Fig. 1d) for

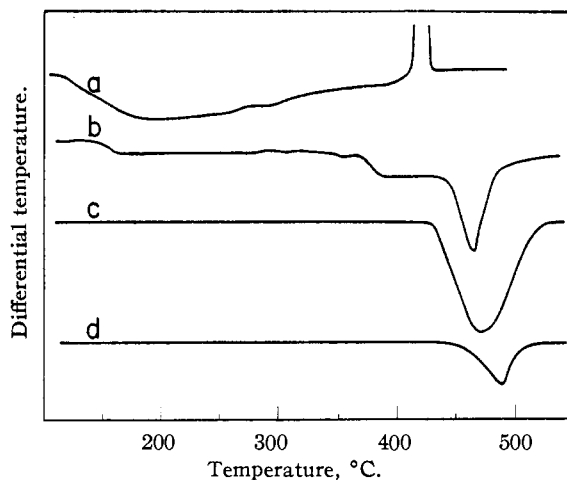


Fig. 1.—Differential thermal analysis: (a) hydrous oxide dried at 25° in a vacuum for 12 hr., (b) hydrous oxide and CrOOH, (c) CrOOH, (d) CrOOH and cubic oxide.

a product containing CrOOH and cubic oxide shows no exothermic effect, but the endothermic effect is smaller due to the dilution of CrOOH and possibly also to the superposition of a slight exothermic effect. X-Ray diffraction showed that a sample taken immediately after completion of the heat absorption was rhombohedral dichromium trioxide.

In order to ascertain whether or not the origin of the hydrous oxide had an effect on the products, hydrothermal experiments were carried out under the same conditions (393-419° for 40 hr.) with starting materials precipitated from nitrate, chloride and sulfate solutions, and from a solution of chromium(VI) trioxide by hydrazine hydrate. The chromium content of the products varied only from 59.1 to 60.3%. The products gave the X-ray diffraction pattern of CrOOH and, as indicated by line breadth, were of similar crystallinity.

Attempts were made to ascertain if 419-424° might be the CrOOH rhombohedral Cr₂O₃ transition temperature by holding samples of dichromium trioxide with water in the bomb at appropriate temperatures for as long as 260 hours. However, the formation of CrOOH was not detected. Dichromium trioxide made in the hydrothermal bomb and the commercial reagent grade chemical were used as starting materials.

Hydrothermal Experiments in Sodium Hydroxide Solutions.—Table III shows the marked increase in the rate at which CrOOH was formed when water was replaced by dilute sodium hydroxide solutions. The starting material was hydrous oxide precipitated from chloride solution and each product was CrOOH. Products made with water in the bomb, even under the most rigorous conditions, approached the theoretical 61.2% Cr only very slowly and always gave slightly broadened diffraction lines in contrast to the products made in 0.5 M sodium hydroxide solution which gave sharp diffraction lines after only 20 hours.

TABLE III
COMPARISON OF RATES OF FORMATION OF CrOOH IN WATER
AND IN NaOH SOLUTION

Expt.	Soln. in bomb	Temp., °C.	Time, hours	Cr in product, %
10	Water	419	352	60.8
21	Water	419	260	60.6
22	Water	419	164	60.5
23	Water	419	40	60.0
24	Water	419	15	59.5
25	0.5 M NaOH	419	88	61.2
26	0.5 M NaOH	419	43	61.1
27	0.5 M NaOH	419	20	60.7
28	0.5 M NaOH	350-365	90	61.0
29	0.1 M NaOH	350-365	90	60.8
30	Water	350-365	90	60.6

Preparation of essentially pure CrOOH was achieved in several of the experiments reported, for example 25, 26 and 28. The thermal analysis curve (Fig. 1c) is for material of almost theoretical composition. The average density of CrOOH as determined by the displacement method using a 1-cc. pycnometer on samples containing 61.0–61.2% Cr was 4.12 g./cc.

Discussion

X-Ray data for CrOOH indicate that it is not isomorphous with any of the isoformular aluminum, manganese or iron compounds. Iron and aluminum oxyhydroxides are isodimorphous, and goethite (α -MnOOH) also is isomorphous with diaspore and goethite¹² members of the alpha series. However, a second manganese oxyhydroxide, manganite, does not have the same unit cell as boehmite and lepidocrocite which are members of the gamma series¹³; also a third iron oxyhydroxide, β -FeOOH, has been reported.¹⁴ A mineral having the composition CrOOH has been found¹⁵ but from available data¹⁶ it appears to give an X-ray diffraction pattern different from synthetic CrOOH. The arrangement of lines on the X-ray diffraction pat-

tern of CrOOH is somewhat similar to the arrangement of lines in the patterns of lepidocrocite or boehmite, members of the γ -series. An elucidation of the structural relationships among these oxyhydroxides should prove to be a most interesting and important contribution to inorganic chemistry.

Although the data presented do not define stability relations in the system chromium(III) oxide-water, discussion of several experimental facts suggests probable relationships. CrOOH was formed in the hydrothermal bomb at temperatures below 419–424°, and is probably the stable phase below this temperature since it decomposed endothermically at 420–430° in the thermal analysis apparatus to give rhombohedral Cr₂O₃. The cubic oxide may perhaps be regarded as monotropic, as is the cubic gamma iron oxide, since differential thermal analysis curves of mixtures of CrOOH and cubic oxide did not show the second minimum which would be expected for a stable cubic oxide-rhombohedral Cr₂O₃ transition.

Phase relationships in which CrOOH is the stable phase below a transition temperature of 419–424°, rhombohedral Cr₂O₃ is stable above that temperature, and the cubic oxide is a metastable phase, are consistent with the data presented except for the serious difficulty that the rhombohedral oxide could not be converted to CrOOH.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Diamagnetic Anisotropy of Natural and Synthetic Rubbers¹

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The change in anisotropy with elongation has been found for natural rubber and for several synthetic rubbers. Unsaturated rubbers have a large principal susceptibility perpendicular to the direction of stretching, because of the presence of olefinic double bonds. The differences between natural rubber and polybutadiene are attributed to the presence of unsaturated side-groups caused by 1,2-addition in polybutadiene. It is probable that the magnetic anisotropy of these rubbers depends not upon the actual degree of crystallinity of the rubbers, but upon the ability of the long-chain molecules to align themselves parallel to the direction of stretching. Therefore the changes in anisotropy with stretching will be large when there is no cross-linking, and small when cross-linking occurs to any large extent. Saturated rubbers have an anisotropy opposite in sign to that of unsaturated rubbers. This must be caused by the broadening of electronic orbits perpendicular to the direction of stretching. Apparently methyl side-groups cause such a broadening of electronic orbits in polyisobutylenes, an effect much greater than the similar effect in polyethylene.

Introduction

The magnetic anisotropy of rubbers has previously been studied by Mme. Cotton-Feytis.⁴ She first observed that vulcanized commercial rubber showed some anisotropy and studied the effects of compression, stretching, and hot and cold working upon crude rubber. By Krishnan's oscillation method⁵ she measured the anisotropy of stretched rubbers, using rubber bands stretched around a glass or plexiglas disc. The anisotropy was found

to increase in the early stages of elongation, but at 400 to 500% elongation the anisotropy tended toward a limit, the curve of anisotropy as a function of tension having the same general shape as the curve showing variation in intensity of spots in the X-ray diffraction pattern of rubber with tension.⁶

In this work, the changes in diamagnetic anisotropy upon stretching have been measured for natural rubber and for several saturated and unsaturated synthetic rubbers in an attempt to relate the changes in anisotropy with stretching to the degree of orientation of the rubbers.

Experimental Part

Preparation of Samples.—The following rubber samples, and their descriptions, were supplied by the B. F. Goodrich Company, in the form of thin sheets approximately a millimeter thick, between two layers of cellophane. The samples were obtained through the courtesy of Dr. H. P. Brown.

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