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Preparation of γ-(Al,Cr)OOH and of H(Cr,Al)O_2 by Homogeneous Hydrolysis at Elevated Temperatures

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Homogeneous coprecipitation, using no base other than solvent water at 160–250°, has been employed to produce microcrystals of chromium-substituted boehmite, γ-AlOOH, and aluminum-substituted chromous acid, $HCrO_2$. Tests of homogeneity of the solids are described; they form the basis of a discussion of conditions favoring each of the possible phases. New evidence of the inertness of basic chromic "solutions" is presented.

The study and exploitation of transition metal hydroxides and oxides have proceeded along two paths, distinguished by differences in techniques of preparation and in the nature of the most interesting or valuable properties. The hydroxides usually are made at relatively low temperatures as amorphous gels, which dehydrate partially or completely to powdered solids with very large surfaces. The physical and chemical characteristics of many of these materials are history-dependent, and almost infinitely variable. Interest in crystalline oxides and mixed oxides, on the other hand, lies principally in the bulk properties of the lattices. These crystals are prepared at high temperatures and are therefore homogeneous and easily reproducible.

Between these preparative extremes, there exist procedures for obtaining hydrated oxides in crystalline form. In addition to the hydrothermal technique, which can be regarded as accelerated aging of a previously deposited unstable solid, methods based on oxidation–reduction and on homogeneous hydrolysis have been employed for direct formation of solids. These latter reactions may yield metastable phases, depending on the path chosen. Thus, the question arises as to what types of mixed crystals can be prepared under circumstances that do not necessarily lead to thermodynamic equilibrium.

The system Al^{+3}–Cr^{+3}–H_2O has been studied, to find optimum and limiting conditions for obtaining crystalline solid solutions. Some of the reasons for selecting this pair of cations are:

(1) The individual aquo-ions hydrolyze to inert solids of identical stoichiometry, MO_2H, under similar conditions of temperature, concentration, and time.

(2) Cr^{+3} and Al^{+3} are interchangeable, over wide concentration ranges, in many lattices, and a large body of data exists on spectral, magnetic, and other physical effects of such substitution.

(3) Both AlO_2H and CrO_2H exist in at least two modifications, so that factors favoring a given reaction might be observed, and information might be obtained on the nature of some of the soluble precursors of the solid phases.

Diaspore, α-AlOOH, has not been obtained directly from dissolved species, but boehmite, γ-AlOOH, can be produced either through oxidation of aluminum by steam or hot water,[1] or by hydrolysis of Al^{+3} above 100°.[2] Even at reflux temperature, some γ-AlOOH is formed hydrolytically, along with (and perhaps by dehydration of) γ-$Al(OH)_3$.[3] The chromic isomorph of boehmite, γ-CrOOH, has been made by reaction of aqueous CrO_4^{-2} with sulfur or sodium formate,[4,5] but reduction of CrO_3 by water leads to a solid composed mainly of chromous acid, $HCrO_2$.[6] This is also the phase which results from hydrothermal treatment of chromic hydroxide,[7] or from hydrolysis of $Cr(H_2O)_6^{+3}$ at reflux[8,9] or higher temperatures.[3,10] Thus, since the phases which seem to form most readily are not isomorphous, inhomogeneity in mixed products might be detected by X-ray or infrared techniques.

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[1] R. Fricke and K. Jockers, *Z. Naturforsch.*, **2b**, 244 (1947).

[2] (a) W. Ipatiew and B. Muromzew, *Ber.*, **60**, 1980 (1927); (b) W. Ipatiew, *ibid.*, **63**, 2365 (1930).

[3] J. A. Laswick, unpublished observation.

[4] German Patent No. 492,684.

[5] F. Hund, *Naturwiss.*, **46**, 320 (1959).

[6] B. J. Thamer, R. M. Douglass, and E. Staritzky, *J. Am. Chem. Soc.*, **79**, 547 (1957).

[7] A. W. Laubengayer and H. W. McCune, *ibid.*, **74**, 2362 (1952).

[8] N. Bjerrum and C. Faurholt, *Z. physik. Chem.*, **130**, 584 (1927).

[9] J. A. Laswick and R. A. Plane, *J. Am. Chem. Soc.*, **81**, 3564 (1959).

[10] J. A. Ibers, C. H. Holm, and C. R. Adams, *Phys. Rev.*, **121** 1620 (1961).

Experimental

All solutions were prepared from reagent grade compounds and distilled water which had been further deionized with a mixed-bed ion exchanger. Forty-ml. samples were sealed, without replacement of enclosed air, in Pyrex tubes of 18 mm. inside diameter and approximately 55-ml. capacity; these were protected during heating by being sealed in a stainless steel bomb partially filled with water. Heating was accomplished electrically and controlled to within about 2°. Reaction temperatures were reached in 3–4 hr., on the average, and maintained for 2–3 days. Quenching was hastened by use of an air stream to remove heat from the shell, and samples could be removed within 1 hr. after completion of a run; most of the temperature drop obviously occurred during the first minutes. The apparatus was agitated during part or all of some runs, although no effect on the products was observed.

As a precaution against possible accumulated gaseous products, each tube was vented by application of a pointed flame near the top, prior to being cut open. Normally the venting was inward, sometimes with slight contamination of the solid products; for this reason, silicon analyses are valid only as maximum values.

Acidities were determined by conductometric titration with standard NaOH solution. Other analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Reflectance spectra were measured with a Beckman Model DU spectrophotometer with reflectance attachment. Debye–Scherrer patterns of the crystalline products were prepared by the Research Services Section of this Institute; a Philips camera of 114.6 mm. diameter was used with CuKα radiation and Ni filter. The same Section provided infrared data on samples by the KBr-pellet technique.

Results and Discussion

Reaction Conditions.—As mentioned above, both γ-AlOOH and $HCrO_2$ have been prepared at 100°, but formation times were prohibitively long. The use of higher temperatures led to somewhat better crystallized products and greater yields, as well as very much faster rates. Optimum conditions gave crystallite diameters of about 500 Å. for boehmite and 1000 Å. for $HCrO_2$. The improved crystallinity may be principally a result of the higher acidities present when the higher temperatures are achieved.

This effect of acid was noted by Ipatiew,[2a] who also reported[11] a wall effect in CrO_3 reduction in quartz, in the presence of H_2SO_4. In the present investigation, some products, especially substituted boehmites, adhered tightly to the tubes in which they formed. This was particularly true in solutions containing high concentrations of chloride or bromide ion. Packing reaction tubes with glass wool caused faster deposition of solids, which then tended to be nearly amorphous.

To minimize depletion of the mother liquor, especially in mixed systems, reactions usually were limited to 25° temperature intervals. Thus, most samples were filtered after initial heating to 200°, resealed, and reaction permitted to proceed at 225°. The process was repeated for final equilibration at 250°. Typically, about 4–8% of the available Cr^{+3} and 10–20% of the Al^{+3}, in chloride solutions, were converted to solid MOOH in each interval. The Al:Cr ratio in solution thus tended to decrease, with increasing temperature, but the ratio in the crystals was not greatly affected, since the temperature coefficient of solubility of γ-AlOOH is *apparently* more negative than that of γ-CrOOH. (Alternatively, this may merely reflect the greater complexing of Cr^{3+} by chloride[12] at the higher temperature.)

Above 250°, increasing amounts of silicon were found in the products. At 280°, significant devitrification of the containers occurred, and kaolinite or its chromic analog sometimes formed in sufficient quantity to be readily detectable by X-ray and infrared techniques. Most of the materials studied therefore were prepared in the 200–250° range. Silica analyses then averaged 3 to 10% (but see Experimental section).

This inclusion of silicon logically demanded that reaction times be minimized. Fortunately this did not conflict with the experimental goals, since ripening, or elimination of lattice imperfections, was not desired as a means of obtaining larger crystallite dimensions. Thus, heating was normally done for 2 or 3 days, beyond which no precipitation occurred, and evidence will be given below to show that rearrangement in the solid phase could not have been significant during these periods; rather, the properties of the solids can be taken as indicative of their initial modes of deposition.

Media.—Since the net reaction liberates three protons for each cation deposited, solid formation (yield) is favored by dilution. In addition, it was found that too high cation concentrations generally led to poorly defined products. In terms of crystallite dimensions, ease of filtration, and certain empirical infrared criteria, the best boehmites, for the range of conditions employed, were obtained from solutions less than 0.05 *M* in Cr^{+3} and 0.15 *M* in Al^{+3}. Chromous acid

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[11] W. Ipatiew and A. Kisselew, *Ber.*, **59**, 1418 (1926).

[12] H. S. Gates, Thesis, Univ. of Wisconsin, 1956; University Microfilms Document No. 16,163.

crystallinity was relatively unaffected by cation concentrations up to 0.2 *M*.

Obviously, these values are not independent of the other ions present. Indeed, a number of interesting synthetic minerals were prepared in the course of a fruitless search for an "inert" medium which was to have served for maintaining constant ionic strength. The experiments described here used chlorides and nitrates as starting materials, sometimes with added bromide or boric acid, which did not affect the gross composition of the solids.

Aluminum solutions without Cr^{+3} yielded boehmite in all cases; the product from chloride was less crystalline than that from nitrate. In the case of chromium, nitrate solutions, or chloride with added nitrate or with a very low concentration of Cr(VI), led to well defined $HCrO_2$, whereas chloride solutions protected from oxidation yielded a nearly amorphous material, perhaps partly γ-CrOOH.

When both Cr^{+3} and Al^{+3} were present, within the limits mentioned above, chloride solutions led to one detectable phase, γ-(Al,Cr)OOH; nitrates, or solutions with large amounts of Cr(VI)—0.01 *M* or more—produced crystalline $H(Cr,Al)O_2$. The fact of substitution was easily established by X-ray diffraction techniques, showing lattice expansion on introduction of Cr^{+3} into boehmite, and the converse for the chromous acids. The boehmites also exhibited the characteristic pink-green color series for increasing occupancy by Cr^{+3} or Al^{+3} sites in octahedra of oxygen atoms,[13] with an unexpected intermediate range of pure blue. The Al-substituted chromous acids showed, to the unaided eye, somewhat the same muddy brown-gray color as pure $HCrO_2$, but a regular trend was evident in their reflectance spectra.

Chloride solutions with over 25 mole % Cr^{+3} yielded boehmites that were distinctly less crystalline, but there was no evidence of $HCrO_2$ formation. Rather, it appeared that amorphous material was deposited in the absence of sufficient boehmite nuclei. Likewise, in the reactions leading to chromous acid, a comparatively large amount of oxidant was needed to prevent formation of boehmite. Even then, an Al:Cr ratio of 20 led to formation of γ-AlOOH in large quantity, apparently mixed with substituted $HCrO_2$.

The inclusion of appreciable amounts of Al^{+3} in $HCrO_2$ from nitrate solutions was achieved only by utilizing high Al:Cr starting ratios. For example, from a ratio of one, both cations 0.12 *M*, only 5% substitution of Al^{+3} occurred. Increasing the ratio to 4 resulted in 14% substitution. Here, the opposing tendency of Al to form the boehmite lattice may be at least as much a limiting factor as the ability of the $HCrO_2$ lattice to accommodate large proportions of Al^{+3}. One product showed a net Al content of 35 mole %, but there was no certainty that it was entirely present in the $HCrO_2$ lattice. Not unexpectedly, this material was least crystalline of all those prepared, and its reflectance spectrum did not fall readily into line with those of the more well defined samples. The presence of boehmite was not detectable, either by its infrared absorption at 1070 cm.$^{-1}$, or by its powder diffraction pattern.

In the boehmites, evaluation of uniformity was accomplished somewhat more confidently, on the basis of a large body of consistent data and the greater accuracy of reflectance spectra of the less intensely colored specimens, together with the unusual sensitivity of the human eye to subtle variations in the characteristic Cr^{+3} visible spectrum. Tables I and II give typical compositions of chloride solutions and their products at 225 and 250°, respectively.

Solutions were made for 200° pre-equilibration with Al:Cr ratios from 0.6 to 15, total cation molarities from 0.10 to 0.21, containing 0.002 to 0.025 *M* added HCl, and, in some cases, 0.1 to 0.5 *M* KNO_3, KBr, H_3BO_3, or excess KCl, or trace quantities of CrO_3. Chloride seemed more effective than bromide in holding Cr^{+3} in solution, while boric acid seemed to lead to products higher in Cr than would have been expected. Unlike $HCrO_2$ preparations with excess Al^{+3}, no tendency to form a second crystalline phase was observed as Cr^{+3} content increased, in the absence of oxidizing agents; rather, a gradual increase in amorphous content was noted. Chromium(VI), including that formed by reduction of nitrate, caused greater deposition of Cr^{+3}, even in cases where only γ-(Al,Cr)OOH was directly detectable.

The Debye–Scherrer pattern of one such product, with 23 mole % Cr, displayed a strong 4.5 Å. line attributed to $HCrO_2$, in addition to the characteristic lines of γ-AlOOH. A similar pattern was obtained from the product of the 20:1 (nitrate only) solution mentioned above,

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[13] See, *e.g.*, O. Schmitz-DuMont and D. Reinen, *Z. Elektrochem.*, **63**, 978 (1959).

TABLE I

COMPOSITIONS OF TYPICAL CHLORIDE SOLUTIONS AND 225° PRODUCTS

Concn. before heating			Mole % Cr in solid	R	$[Cl^-]$	Other ions; remarks
[Al]	[Cr]	$[H^+]$				
0.096	0.0082	0.016	2.39	0.25[a]	0.34	
.082	.0069	.062	2.83	.33[a]	.34	
.086	.0041	.056	2.94	.62	.34	0.0005 Cr(VI)
.089	.014	.041	3.54	.22	.37	.0005 Cr(VI)
.090	.015	.037	5.40	.33	.37	
.188	.025	.010	7.51	.59[a]	.69	
.125	.025	.010	9.13	.47[a]	.50	
.125	.025	.010	10.2	.56	.50	.5 Br^-
.121	.025	.021	10.6	.55[a]	.50	
.125	.025	.010	14.6	.85	.50	.1 NO_3^-
.125	.042	.013	19.1	.69[a]	.58	
.125	.042	.011	21.4	.82[a]	.58	
.047	.073	.065	56.5	.82	.43	Amorphous by X-ray

[a] Homogeneous products (see text).

TABLE II

COMPOSITIONS OF TYPICAL CHLORIDE SOLUTIONS AND 250° PRODUCTS

Concn. before heating			Mole % Cr in solid	$\frac{[H^+]^3}{[Al]} \times 10^2$	R	$[Cl^-]$	Other ions; remarks
[Al]	[Cr]	$[H^+]$					
0.125	0.0083	0.015	1.85	0.42	0.32[a]	0.92	
.080	.0039	.076	2.09	2.53	.38	.34	0.0005 Cr(VI)
.125	.0083	.010	2.58	1.17	.37[a]	.45	
.079	.0077	.066	2.80	1.81	.26[a]	.34	
.125	.0083	.015	2.93	0.69	.48[a]	.42	.5 Br^-
.077	.0067	.076	3.08	3.20	.30[a]	.34	
.125	.0083	.015	3.56	1.31	.45[a]	.42	.5 H_3BO_3
.125	.0083	.015	4.37	2.09	.90	.42	.1 NO_3^-
.082	.015	.061	5.92	3.02	.30[a]	.37	
.113	.024	.049	7.11	0.58	.33[a]	.50	
.121	.025	.023	10.1	0.32	.56[a]	.50	.5 Br^-
.116	.040	.045	12.9	1.35	.38[a]	.58	
.075	.022	.063	15.6	3.88	.47[a]	.37	.1 H_3BO_3
.085	.033	.042	18.1	2.55	.46[a]	.43	.1 H_3BO_3
.075	.04	.061	39.6	3.91	1.0	.43	.1 H_3BO_3

[a] Homogeneous products (see text).

although the gross Cr content was only 8 mole %.

Significantly, both of these materials were anomalously colored, and from this starting point, it was found possible to correlate spectra of various other solids with oxidizing conditions of preparation, eliminating uncertainties which otherwise would have existed in the absence of Debye–Scherrer lines or other identifying features. (Detection of $HCrO_2$ in boehmite by its most conspicuous infrared absorption, a rather weak 1200 cm.$^{-1}$ band, was unsatisfactory.) When these exceptional products had been categorized, it was found that still another form of evidence tended to verify the homogeneity of the remaining materials, namely, the near constancy of the ratio

$$R = \frac{[Al]}{[Cr]} \times \frac{N_{Cr}}{N_{Al}}$$

in Tables I and II, where N_{Cr} and N_{Al} represent the mole fractions of CrOOH and AlOOH, respectively, in the substituted boehmites. These values are calculated for room temperature molarities, and ignore solution variables as olation, chloro-complex formation, and changes in ionic strength, as well as activity coefficients in the solids, factors which cannot be evaluated for the temperatures involved. Samples judged to have yielded one homogeneous solid phase, using the criteria of instrumentally or visually determined color, regardless of method of preparation, are marked with a superscript *a*. Most values which deviate appreciably probably are explained by added bromide, H_3BO_3, etc., as noted. The preceding column in Table II, $[H^+]^3/[Al]$, is given merely to show the wide variations which result when the data are treated as a simple equilibrium of saturated solution with a solid phase of constant activity, *viz.*

$$Al^{+3} + 2H_2O \rightleftharpoons AlOOH_{(s)} + 3H^+$$

History Dependence.—Several experiments were designed to learn the fate of colloidal species previously shown[9] to form on addition of base to chromic solutions. Essentially, these preparations involved pairs of samples of identical net composition, mixed in different orders such that only one combined Cr^{+3} and NaOH, which were boiled prior to addition of the remaining ingredients. In no case were the 200° products the same, and in some instances the difference persisted even to 225°.

For example, two solutions were prepared in the following manner: for the first, 1.06 mmoles of NaOH and 1.0 mmole of $CrCl_3$, in about 30 ml., were boiled 1 hr. (without precipitation) and cooled; then 2.0 mmoles of HCl, 0.52 mmole of NaOH, and 7.5 mmoles of $AlCl_3$ were added and the volume adjusted to 40 ml. For the second, the $AlCl_3$ and entire 1.58 mmoles of NaOH were boiled together, cooled, and the HCl and $CrCl_3$ were added. The first solution was clear green, the second, clear blue. Both were heated to 200° for 40 hr., but no precipitate formed in either. After further heating at 225° for 64 hr., the first held 39 mg. of solid containing 7.5 mole % Cr and giving a sharp Debye–Scherrer pattern of (distorted) boehmite. The second contained 3 mg. of solid, which was not analyzed. After final equilibration at 250° for 72 hr., the new solid in the first totaled 10 mg., in the second, 76 mg. The first filtrate had Al:Cr = 7.8; in the second, the ratio was 6.8.

Similarly, a series of three samples led to deposition below 200° of 1.8% of the available Cr when $CrCl_3$ was not originally boiled with NaOH, 9.0% when it was (0.8 OH^- per Cr), and 13.9% when the Cr^{+3} and NaOH were boiled together with a trace (5×10^{-4} *M*) of Cr(VI) (not present in the first two) prior to mixing of the other ingredients.

The behavior of solutions pre-treated with base was unpredictable, and no generalizations will be attempted, but the remarkable inertness of these "dissolved" basic species is worth noting.[14] One is led to inquire whether the solids from these experiments could be considered homogeneous, or whether two separate phases might not coexist. In point of fact, a few samples, formed below 200°, had colors intermediate between those of the true boehmites and the materials thought to contain $H(Cr,Al)O_2$, but the 225 and 250° products apparently were well defined Cr-boehmites (some are included in Tables I and II). One explanation would be that $HCrO_2$ formation is enhanced by elevation of pH, although the primary effect of the base, described above, was formation of extremely inert colloidal species.

Conclusions.—The formation of $HCrO_2$ in preference to γ-CrOOH indicates the relatively greater stability of the former. Similarly, boehmite has been described as metastable with respect to its polymorphic modification, diaspore,[15] at the temperatures and pressures involved here. Nevertheless, it has been possible, by appropriate choice of conditions, to co-crystallize the γ-forms in good purity. In principle, it would seem that suitable conditions might be found for obtaining other solid solutions through the hydrolysis of pairs of cations having like charges, similar ionic radii, and suitably slow rates of solution of the product oxides.

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[14] *Cf.* H. W. Kohlschutter and O. Melchior, *Angew. Chem.*, **49**, 865 (1936).

[15] G. C. Kennedy, *Am. J. Sci.*, **257**, 563 (1959).