Chromium Compounds on Silica Gel

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Abstract: The physical and chemical states of a series of chromium compounds deposited on wide-pore silica gel have been studied, principally by epr and optical absorption spectroscopy. The compounds or complex ions have been deposited by ion exchange, by impregnation, and by adsorption. As judged by epr, $Cr(NH_3)_6(NO_3)_3$ and $Cr(H_2O)_6(NO_3)_3$ in aqueous solution are in the same environment in bulk solution as in solution impregnated into the pores of silica gel. Ion exchange of the hexaammine onto the surface of the gel leads to considerable broadening of the epr absorption, and removal of pore water leads to still further broadening. These line broadenings reflect increasingly restrictive binding. Desiccation of gel containing ion-exchanged hexaammine promotes decomposition to surface chromia polymer. Very similar polymer is produced by reactions of many other chromium compounds deposited on silica gel. Monomeric Cr(III) complexes are unstable *vs.* polymer but they were observed in a few instances. Cr^{2+} ion-exchanged onto silica gel is stable at room temperature to water, but it is rapidly oxidized by air to Cr(VI), Cr(V), and polymer. Cr(II) prepared by reduction of polymer at 450–500° is oxidized by both water and air at 22°. Oxidation by air is rapid even at −78° but no Cr(III) is then detectable by epr at 22°.

Chromium compounds deposited on alumina, silica–alumina, and silica have been extensively investigated recently by means of electron paramagnetic resonance (epr). These materials are interesting in themselves, and they are important as catalysts in various reactions involving hydrocarbons and hydrogen and in the polymerization of ethylene.

Epr spectra have been interpreted as characterizing several types of surface complexes. A broad line at $g = 2$ has been ascribed to Cr^{3+} in microparticles of chromia.[1,2] It is also observed in chromia gel.[3] Two absorption lines have been assigned to Cr^{3+} in solid solution in alumina. As might be expected such absorptions are missing with silica.[4] Alumina and chromia are completely miscible in solid and liquid phases whereas chromia and silica are immiscible even in the liquid phase[5] presumably because Cr(III) is most stable in sixfold coordination and Si(IV), in fourfold.

In addition, an absorption ascribed to Cr^{5+} has been extensively studied owing to its possible relation to activity for ethylene polymerization. The degree of asymmetry of this rather sharp absorption line appears to be particularly sensitive to the geometric environment.

Most of the materials previously studied were prepared by impregnating alumina, silica–alumina, or silica with an aqueous solution of chromic anhydride followed by drying and heating. In the last step much of the CrO_3 decomposes to Cr_2O_3.

Since silica behaves as a weak acid ion exchanger,[6] one should be able to prepare silica covered uniformly with cationic chromium complexes. This procedure would avoid that deposition of crystallites in the pore structure of the support which necessarily occurs during the drying of impregnated catalysts. In addition, in ion exchanging cations onto silica to form $\equiv SiO^-M^+$, one avoids the introduction of anions which necessarily attends impregnation by solutions of salts of Cr(III) or Cr(II).

We have studied a variety of chromium complexes on silica. Most were prepared by ion exchange but some by impregnation. Our purpose in this paper is the characterization, primarily by epr and optical spectroscopy, of the state and chemical reactivity of various chromium species on the surface of silica. We have used a wide-pore silica, Davison grade 70, reported pore diameter 140 Å, surface area 340 m^2/g, and porosity 1.16 cc/g. This material would contain about 3 moles/g of surface silanol groups, $\equiv SiOH$.

One can use silica as an ion exchanger in two ways.[6] One may expose silica to a basic solution containing the ion to be deposited. The reaction may be written

$$\equiv SiOH + M^+ + OH^- = \equiv SiO^-M^+ + H_2O$$

The most convenient base seems to be ammonium hydroxide at a pH of 10–10.5. Of course, some ammonium ion may also be bound to the surface. In the second method, one adds a 0.01 *M* solution of sodium hydroxide to silica gel to a pH of 10.5 and then washes the gel with many changes of water. The resultant gel contains about 0.2 mmole of Na^+/g. Treatment with a solution of M^+ results in ion exchange.

Unfortunately, neither method permits deposition of $Cr(H_2O)_6{}^{3+}$. In the first method, chromium oxide gel precipitates in the treating solution. In the second, the following reaction predominates.

$$\equiv SiO^-Na^+ + Cr(H_2O)_6{}^{3+} = \equiv SiOH + Na^+ + Cr(H_2O)_5OH^{2+}$$

In fact, no material as acidic as $Cr(H_2O)_6{}^{3+}$ can be ion-exchanged onto silica. The pK_a of the hexaaquo ion is 3.8,[7] whereas that of the silanol group is about 9. We can, however, readily deposit the much less acidic ammine complexes of Cr(III) and the aquo complex of Cr(II).

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[1] D. E. O'Reilly and D. S. McIver, *J. Phys. Chem.*, **66**, 276 (1962).

[2] L. L. van Reijen, W.M.H. Sachtler, P. Cossee, and D. M. Brouwer, "Proceedings of the Third International Congress on Catalysis," Vol. 2, North-Holland Publishing Co., Amsterdam, 1965, p 829.

[3] Yu. I. Pecherskaya, V. B. Kazanskii, and V. V. Voevodskii, *Kinetics Catalysis* (USSR), 3, 90 (1962).

[4] I. V. Aleksandrov, V. B. Kazanskii, and I. D. Mikheikin, *ibid.*, **6**, 383 (1965).

[5] "Gmelins Handbuch der Anorganischen Chemie," Vol. 52, Part B, 8th ed, Verlag Chemie, Weinheim, 1962, pp 50, 52.

[6] R. L. Burwell, Jr., R. G. Pearson, G. L. Haller, P. B. Tjok, and S. P. Chock, *Inorg. Chem.*, **4**, 1123 (1965).

[7] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1967, p 32.

Experimental Section

Materials. Davison grade 70 silica gel was crushed and sieved to 40–60 mesh, washed with 0.1 *M* hydrochloric acid for several hours and then with water, and dried at 140°. The material gave no background in epr. $Cr(NH_3)_6(NO_3)_3$ and $Cr(en)_3Cl_3$ were prepared by standard methods.[8] $CrCl_2(H_2O)_4Cl \cdot 2H_2O$ was prepared following Bjerrum[9] and used as soon as possible. For conversion to $CrCl_3(H_2O)_3$ it was dried over sulfuric acid and dissolved in acetone; the acetone was evaporated and $CrCl_3(H_2O)_3$ was extracted into ether.[10]

A solution of polymeric chromium hydroxide[11] was prepared by dissolving chromium hydroxide precipitated by the urea method[12] in dilute nitric acid. The polymeric cation readily exchanges with $\equiv SiO^-Na^+$. The weight-average molecular weight of one sample of the polymer as determined by ultracentrifugation was 11,700.

Deposition of Chromium Complexes. Complex cations were deposited on silica by either of the methods described in the introductory section, ion exchange with silica pretreated with sodium hydroxide or by stirring silica in a solution of the complex cation and ammonium hydroxide. Resulting concentrations of the complex ion usually were about 0.2 mmole/g. After washing, the silica was exposed to the vacuum of a water aspirator at room temperatures. This gave a *superficially dry* gel which contained about 40% by weight of water in the pores. From the reported porosity of the silica gel, 1.16 cc/g, one computes that the gel, in which the pores were completely filled, would contain 54% by weight of water.

Some gels were prepared by impregnation. A solution containing the desired complex was added to the gel. If the volume of the solution was less than that of the gel porosity, the resulting material appeared dry. If more solution than this was used, residual solution was removed by blotting with filter paper.

The chromium content of gels prepared by impregnation could be immediately extracted by water; that of those prepared by ion exchange could be extracted by 0.1 *M* hydrochloric acid but not by water.

The neutral complex, chromium trisacetylacetonate, is readily adsorbed from its solution in carbon tetrachloride. However, $Cr(H_2O)Cl_3$ is not readily adsorbed from ether.

Spectra. Epr spectra were determined on a Varian V-4500 instrument with a 6-in. electromagnet, a Klystron frequency of 9.19 kMHz, and a modulation frequency of 100 kHz. Samples were usually contained in a 4-mm quartz tube sealed under vacuum or closed by a Nupro bellows valve. Solutions and gels with high water content were examined in a Varian quartz cell of thin rectangular cross section designed for aqueous solutions. Optical spectra were determined on a Cary spectrometer, Model 11 or 14. The gels were immersed in carbon tetrachloride or, for gels of high water content, in heptane.[6]

Analysis. Gels were analyzed for chromium by thrice repeated treatment with boiling 1 *M* nitric acid. Hydrogen peroxide was added to the combined extracts. After making the solution basic, its chromate content was determined by absorption spectroscopy at 3720 Å. The chromate content of gels, which already contained chromate, was first determined by extraction with water and then with 0.1 *M* sodium hydroxide. The extract was made neutral, the precipitate of silica removed, and the solution made basic and analyzed spectrophotometrically.

Silica and Cr(III). The complex ion $Cr(NH_3)_6^{3+}$ proved to be of particular interest. In agreement with McGarvey,[13] its epr absorption in aqueous solution has a half-width of 33 G. Table I reports half-widths of the ion impregnated into and ion-exchanged on silica gel. Similar data for $Cr(NH_3)_5Cl^{2+}$, $Cr(H_2O)_6^{3+}$, $Cr(H_2O)_4Cl_2^+$, and the polymeric chromia cation are also given in Table I. All lines were symmetric except that for $Cr(H_2O)_4Cl_2^+$ which was slightly asymmetric. This complex ion hydrolyzes rather rapidly.[13] The listed values are the initial ones.

The optical absorption spectrum of a complex ion is, in general, the same in solution, as impregnated, and as ion-exchanged.

Table I. Half-Widths in Gauss of Epr Lines at 22°

Complex	g^d	Aq soln	Water–glycerol soln	Silica gel ion exchanged	Impregnated silica gel
$Cr(NH_3)_6^{3+}$	1.98	33	134	90–100	35[b]
$Cr(NH_3)_5Cl^{2+}$	1.95	140	. . .	400	. . .
$Cr(H_2O)_4Cl_2^+$	1.97	350	. . .	. . .[a]	345[c]
$Cr(H_2O)_6^{3+}$	. . .	148	282	. . .[a]	148[b]
Polymer	1.97	340	460	460	. . .

[a] The cation is too acidic for mere ion exchange. [b] Impregnated as a solution of the nitrate. [c] Impregnated as a solution of the chloride. [d] In aqueous solution.

$Cr(en)_3^{3+}$ exhibits no epr absorption spectrum in solution at 22°, but, ion-exchanged onto silica gel, it shows a line at $g = 4$ in the X band. In the solid state, as the chloride powder, it absorbs at $g = 1.98$, half-width 330 G.

To observe the effect of restriction upon molecular motion, the epr spectra of several ions were determined in a solution of glycerol and water, 2:1 by volume. Results are given in Table I. The absorptions of $Cr(NH_3)_6^{3+}$ and $Cr(H_2O)_6^{3+}$ are broadened but remain symmetrical. That of the polymeric cation is somewhat broadened. At −195°, $Cr(en)_3^{3+}$ exhibits two lines at low field and an asymmetric one at $g = 2$, although it exhibits no absorption at 22°. $Cr(H_2O)_6^{3+}$ and $Cr(NH_3)_6^{3+}$ exhibit one line each at $g = 2$. The lines are sharper than at 22° but asymmetric. Upon cooling from 22 to −195°, the line from the polymeric cation remains symmetric but broadens to 730 G.

As shown in Figure 1, desiccating the gel ion-exchanged with hexaammine widens the epr absorption to about 240 G and leads to the appearance of some asymmetry. Desiccation was effected by washing the gel with methanol and then carbon tetrachloride. Epr spectra were determined on gel immersed in carbon tetrachloride or chloroform. Evacuating the gel at 10^{-2} mm for several hours gives similar results. The exact degree of broadening is not very reproducible in these experiments. Restoration of water by reverse washing in the first case or by simple addition of water in the second restores the epr spectrum to its initial form. If the gel is now extracted by 0.1 *M* hydrochloric acid, the extract exhibits the original spectrum of hexaammine.

Gel prepared by impregnation with a solution of the hexaammine nitrate gave the same half-width at concentrations of 0.2 and 0.06 mmole/g. Upon desiccation, the half-width became 520–540 G. The half-width of hexaammine nitrate powder is 620 G.

The epr spectra of $Cr(acac)_3$ are rather complicated. Spectra similar to that of the powdered solid are shown by $Cr(acac)_3$ on silica and in benzene solution (0.16 *M*). The line on the gel is broader and that in benzene solution, broader still. The absorption maximum of the solid at $g = 3.85$ shifts to 3.68 on the gel and 3.10 in solution.

Reactions of Cr(III) on Silica. The hexaammine ion ion-exchanged onto silica gel hydrolyzes very slowly when the gel is kept in the superficially dry state in the dark, about as fast as in solution. Any treatment which removes pore water augments the rate of decomposition. The color changes from the initial yellow through pink, gray, and purple and finally to green if the gel stands in a desiccator for several days, if it is evacuated by a mercury diffusion pump, or if dry nitrogen is passed over it. Under the same conditions of partial desiccation, impregnated gel decomposes much more slowly than the ion exchanged. Use of a mixture of nitrogen and ammonia, 5:1, slows the decomposition of the ion-exchanged hexaammine *vs.* dry nitrogen but much less than does addition of water vapor to 4.5 mm. In the latter case, the rate is hardly above that of stored, superficially dried gel. The epr spectrum of the purple gel obtained by treatment at 25° exhibits an asymmetric line at $g = 1.97$, half-width of 350–450 G, and two broad components at lower fields. Visible spectra are shown in Figure 2.

Five days after preparation, an ion-exchanged hexaammine gel kept in the superficially dry state exhibits evidence for new species. Extraction of the gel with 0.1 *M* HCl removes hexaammine (37% of total chromium) and leaves a material with absorption maxima at 4250 and 5870 Å. This spectrum resembles that of hexaammine gel dried at 110°. For comparison, absorption maxima of the polymeric cation in solution at pH 4.2 appear at 4250 and 5930 Å; after deposition on the gel and drying at 110°, maxima appear at 4240

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[8] A. L. Oppegard and J. C. Bailar, Jr., *Inorg. Syn.*, **3**, 153 (1952); C. L. Rollinson and J. C. Bailar, Jr., *ibid.*, **2**, 198 (1951). The ligand, ethylenediamine, is represented by en.

[9] N. Bjerrum, *Z. Physik. Chem.*, **59**, 339 (1907).

[10] A. Recoura, *Compt. Rend.*, **194**, 229 (1932).

[11] M. Amat, J. Duclaux, and C. Cohn, *Bull. Soc. Chim. France*, 1217 (1961).

[12] G. Pass, A. B. Littlewood, and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **82**, 6281 (1960).

[13] B. R. McGarvey, *J. Phys. Chem.*, **61**, 1232 (1957).

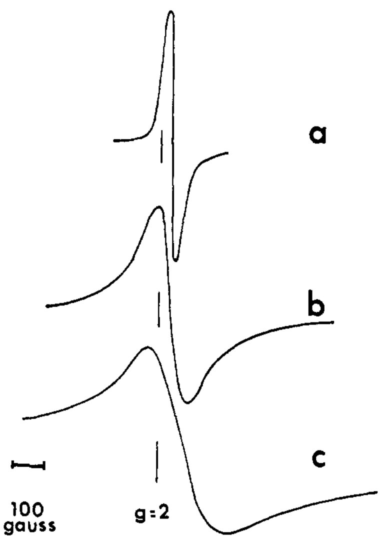

Figure 1. Epr spectra at 22° of $Cr(NH_3)_6^{3+}$: (a) 0.052 M solution in water; (b) ion-exchanged onto silica gel, superficially dry; (c) as in (b) but washed with methanol and then chloroform, 0.125 mmole of Cr/g of dry gel.

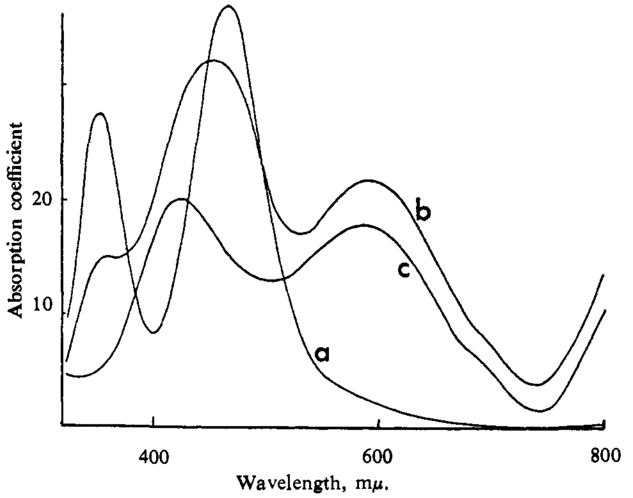

Figure 2. Absorption spectra of $Cr(NH_3)_6^{3+}$ ion-exchanged onto silica gel: (a) freshly prepared, superficially dry; (b) as in (a) but after 5 days at room temperature; (c) after extraction of (b) with 0.1 M hydrochloric acid.

and 6020 Å. The epr spectra of this and of the hexaammine gel dried at 110° are shown in Figure 3. The line at $g = 2$ is nearly the same in both, but the gel prepared from hexaammine shows two more absorptions with maxima at 1400 and 2700 G.

The two lower field absorptions disappear upon heating the gel in air at 140° for 1 day. However, this is accompanied by some oxidation to Cr(VI). If one starts with freshly prepared hexaammine gel, the chromate content after treatment at 140° for 1 day is 40% of the original chromium content. Gels which have been aged at room temperatures show less chromate. The absorption maximum of the Cr(VI) on the gel seemed to vary with concentration being 3640 Å at 0.19 mmole of Cr/g and 3770 Å at 0.02 mmole of Cr/g.

$Cr(NH_3)_5Cl^+$ and $Cr(en)_3^{3+}$ deposited on silica gel behave much like the hexaammine, the former decomposing several times more rapidly and the latter much more slowly. Even at 110° the latter goes only to the purple stage within 1 day.

As judged by optical spectra, $Cr(acac)_3$ adsorbed on silica gel decomposes finally to the same product as that obtained from the hexaammine but much more slowly. Even after treatment with wet nitrogen at 195°, some intermediate product remains as shown in Figure 4.

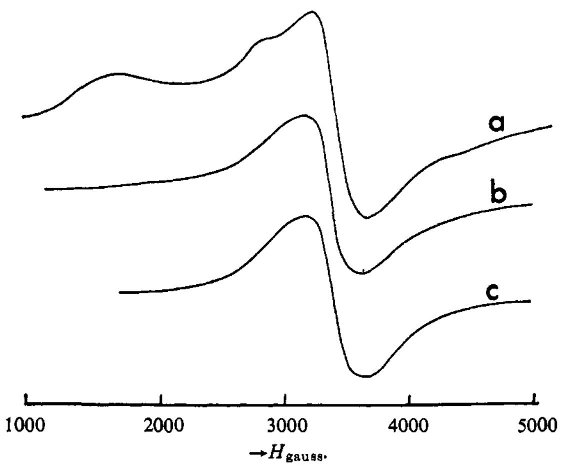

Figure 3. Epr spectra at 22° of Cr(III) on silica gel: (a) $Cr(NH_3)_6^{3+}$ ion-exchanged onto silica gel, heated in air 1 hr at 110°, 0.12 mmole/g of Cr, (b) $Cr(NH_3)_6^{3+}$ ion-exchanged onto silica gel, heated in air 1 day at 140°, 0.19 mmole/g of Cr; (c) chromia polymer ion-exchanged onto silica gel, heated in air 1 hr at 110°, 0.095 mmole/g of Cr. The intensities in curve b have been divided by 2.

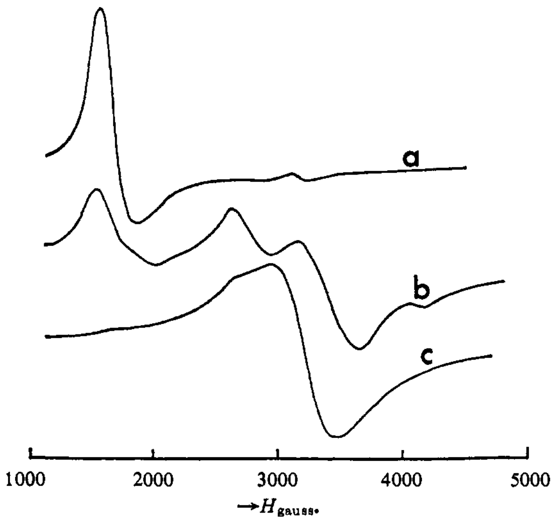

Figure 4. Epr spectra at 22° of $Cr(acac)_3$ on silica gel: (a) prepared by adsorption from solution in carbon tetrachloride; (b) after heating (a) at 195° in a flow of dry nitrogen; (c) after heating at 195° in a flow of wet nitrogen.

Several other preparations lead to a similar product which we identify as polymeric chromia, *i.e.*, some condensation product of $Cr(H_2O)_6^{3+}$ with unspecified degrees of loss of protons. We characterize this polymeric species deposited on silica by optical absorption maxima at about 4250 and 5900–6000 Å, both with extinction coefficients of about 29, and by epr absorption at $g = 1.97$ and a half-width of 400–500 G. For comparison, $Cr(H_2O)_6^{3+}$ in solution absorbs at 4080 and 5745 Å (extinction coefficients of 13.5 and 15.5) and exhibits epr absorption with a half-width of 148 G. The optical and epr absorptions are in accord with those given by Thompson.[14]

For example, if a gel impregnated with a solution of chromium nitrate is exposed to desiccation, nitric acid seems to be lost and a chromia polymer results. As shown in Table II, desiccation over soda lime is particularly effective. Extraction of the superficially dry, impregnated gel with ethyl acetate gives the same result. Extraction of the desiccated gel with 0.1 M HCl does not extract Cr(III) at any substantial rate. Passage of dry nitrogen at 110° over the impregnated gel leads to oxidation of Cr(III) to Cr(VI). Similar

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(14) G. Thompson, Doctoral Dissertation, University of California, Berkeley, June 1964.

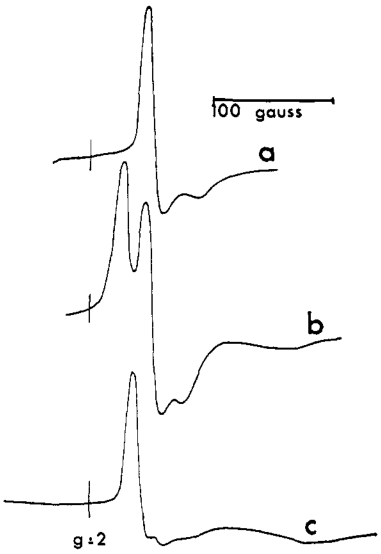

Figure 5. Epr spectra at 22° of Cr(V) on silica gel: (a) $Cr(NH_3)_6^{3+}$ ion-exchanged onto silica gel, heated in oxygen at 250°, 0.11 mmole/g of Cr; (b) $Cr(NH_3)_6^{3+}$ ion-exchanged onto silica gel, reduced by carbon monoxide at 450°, exposed to air at −78°, 0.117 mmole/g of Cr; (c) Cr(II) ion-exchanged onto silica gel, desiccated at room temperature, exposed to air at 22°, 0.086 mmole/g of Cr.

treatment of gel impregnated with $Cr(H_2O)_4Cl_2Cl$ gives a material with the spectroscopic properties of chromia polymer.

Passage of dry hydrogen chloride over the impregnated gels at 110° gives a purple gel which exhibits one epr absorption at g = 1.98, half-width = 160 G, and the absorption spectrum shown in Table II. Since $Cr(H_2O)_3Cl_3$ in ether exhibits an epr line with a half-width of 400 G and absorption maxima at 4900, 6820, and 7100 Å, the purple material probably contains more than three chlorine ions coordinated to each chromium(III) ion, perhaps $H_3O^+[Cr(H_2O)_2Cl_4]^-$ or a chloride-bridged polmeric species. Solid $[Cr(H_2O)_4Cl_2]Cl$ behaves rather similarly but less readily.[15] Water immediately extracts all chromium from the purple gel as the green $Cr(H_2O)_4Cl_2^+$. Treatment of the purple gel or the green gel containing $Cr(H_2O)_4Cl_2^+$ with wet nitrogen at 110° gives a gel which exhibits an epr line at g = 1.97 and a half-width of 440 G characteristic of polymer.

Table II. Visible Spectra of Aquochromium(III) on Silica

Treatment	Wavelength max, Å	
Impregnated, $Cr(NO_3)_3$,[a] superficially dry	4080	5745
In desiccator 12 hr	4130	5790
In desiccator over soda lime 48 hr	4265	5900
Above, after HCl flow at 110°	5200	7380
Polymer by ion exchange, dried at 110°	4240	6020
Polymer in solution, pH 4.2	4250	5930

[a] A dilute aqueous solution exhibits the same spectrum.

Oxidation and Reduction Reactions of Surface Species. If gel upon which hexaammine has been deposited is desiccated by any method and heated at 250° in oxygen, Cr(III) is almost entirely oxidized. Washing with 0.1 *M* NaOH removes over 90% of the chromium. Consequent to oxidation, the broad line epr of polymer disappears and there appears a narrow, asymmetric line of the type ascribed to Cr(V). If the sample tube is alternately exposed to air at 20° and then evacuated, the line shape becomes stabilized to that shown in Figure 5a. Analysis of this spectrum by the method of Ibers[16] gives $g_\perp$ = 1.975 and $g_\parallel$ = 1.955, each with a half-width of 6 G. Double integration of the signal of Cr(V) showed that 13% of the total chromium was present as Cr(V). One might expect this material to be a good catalyst for the polymerization of ethylene.

The hexaammine gel can be reduced by carbon monoxide at 450–500° to give a gel which is pale violet after cooling to room temperatures in carbon monoxide. Dry hydrogen gives rather similar results, but less readily. At room temperatures, no epr lines are detectable. At −195°, two lines near g = 2 and 4 are detectable; both, and particularly the latter, are weak.

Admission of air to the reduced gel even at −78° leads to rapid oxidation to brown gel. The change in color moves through the gel as a sharp boundary. Only 20% of the total chromium is extracted by base from gel which has been oxidized at −78° and then brought to room temperature. The epr spectrum of the material after evacuation is given in Figure 5b. The intensity corresponds to Cr(V) being 2% of the total chromium No signal from Cr(III) could be detected, but its large line width limits detectability to about 10%. If oxidation is conducted at room temperature, Cr(III) (70%) and Cr(V) (1%) are observed by epr and Cr(VI) (32%) by extraction with base. Rapid oxidation at room temperature has been observed before.[2]

In the absence of oxygen, Cr(II) can be readily ion-exchanged onto silica gel pretreated with sodium hydroxide to give a pale blue gel, presumably $[\equiv SiO^-]_2Cr(H_2O)_6^{2+}$. After drying *in vacuo* for 1 hr, exposure to air at room temperatures results in rapid oxidation to a brown gel which exhibits a narrow line ascribable to roughly 4% of Cr(V) (Figure 5c) as well as a broad line characteristic of polymer. Water alone extracted chromate equivalent to 20% of the total chromium content.

Discussion

State of Chromium Complexes When Pores Are Full of Water. The volume per cent void in the wide-pore silica gel which we used is about 70%. The internal porosity of the gel resembles that of a loose gravel bed[17] in which the internal channels have some kind of average diameter in the neighborhood of 140 Å. In the condition which we designate as *superficially dry*, the pores are largely filled with water.

Considering that $Cr(NH_3)_6(NO_3)_3$, $Cr(H_2O)_6(NO_3)_3$, and $Cr(H_2O)_4Cl_2Cl$ impregnated into wide-pore silica gel are immediately extracted by water and considering that the epr spectra of these gels (content in complex about 0.2 mmole/g) are identical with those of the corresponding dilute aqueous solutions, one concludes that the assembly of cations and anions in aqueous solution is little affected by the containing silica surfaces and that the cations can undergo any motions which affect epr line widths about as easily in the porosity as in bulk solution. In particular, our criteria diagnose no difference between the structure of water in bulk and in the porosity of the gel.[18]

In gels prepared by ion exchange, the free nitrate or chloride anions are replaced by $\equiv SiO^-$ groups which constitute part of the surface of the silica. Space charge effects alone would tend to confine the complex ion to the neighborhood of the silica walls. Line widths become broader as shown in Table I. That of $Cr(NH_3)_6^{3+}$ goes from 33 in aqueous solution to 90–100 upon ion exchange into wide-pore silica. That of $Cr(NH_3)_5Cl^{2+}$ also about trebles. The proportionate increase in the polymeric chromia cation is less, an increase from 340 to 460 G. Two factors may contribute to these results. The ions are confined to a region in which there is an asymmetric electric field, and tumbling motions of the ions may be hindered. $Cr(en)_3^{3+}$ which exhibits no epr

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(15) N. Bjerrum, *Ber.*, **40**, 2915, 3949 (1907).

(16) J. A. Ibers and J. D. Swalen, *Phys. Rev.*, **127**, 1914 (1962).

(17) W. G. Schlaffer, C. R. Adams, and J. N. Wilson, *J. Phys. Chem.*, **69**, 1531 (1965). The fundamental particles which constitute the gravel bed in the wide-pore gel are about 100 Å in diameter.

(18) A similar conclusion was reached for faujasites by the more specific technique of pulsed, field-gradient, spin-echo nuclear magnetic resonance: C. Parravano, J. D. Baldeschwieler, and M. Boudart, *Science*, **55**, 1535 (1967).

absorption in solution shows at least one line at $g = 4$ in the X band when ion-exchanged.

Of previous work, our work seems most closely related to that of Nicula, Stamires, and Turkevich,[19] who studied the epr spectrum of cupric ion in synthetic zeolites. They found little difference between the spectrum of the cupric ion in dilute aqueous solution and that ion-exchanged into the fully hydrated zeolite. As compared to wide-pore silica, the channels in the zeolites are much smaller, the number of negative charges per unit surface area of wall are much higher, and there are also many sodium ions present. All of these factors would increase the rate at which copper ions can move into the center of or across a channel. Upon partial desiccation of the zeolite, much more complicated epr absorptions appeared presumably as a result of restrictions upon the motions of the tetraaquocupric ion. Transfer of cupric ion from an aqueous solution to a water–glycerol solution gave broadenings of epr absorptions similar to those shown in Table I.

State of Chromium Complexes in the Absence of Pore Water. Water is strongly adsorbed on silica gel by hydrogen bonding to the silanol groups which cover the surface. Desiccation at room temperatures removes pore water except for the first hydrogen-bonded layer. Heating to somewhat above 100° removes this layer without yet causing substantial condensation of surface silanol groups to siloxane groups.[20,21] Thus, desiccation of ion-exchanged silica gels at room temperatures should remove all but one layer of water molecules.[22] This should result in the much more intimate attachment of cations to the surface siloxy groups with the formation of firm ion pairs.

We have found that replacement of pore water by an inert gas or by an organic solvent of low dielectric constant like carbon tetrachloride results in considerable further broadening of the epr absorption of ion-exchanged $Cr(NH_3)_6^{3+}$ as reported in the text and shown in Figure 1. Restoration of water to the pores returns the epr spectrum to the original form. These results are consistent with considerable restriction to ionic motion attendant upon desiccation. The states of complex ions ion-exchanged in zeolites and in silica gel seem rather similar when pore water has been removed from the adsorbent.

Formation of Surface Polymer. The final product of the decomposition of chromium(III) complexes on a surface of silica is polymeric chromia. If nitrate or chloride salts of $Cr(H_2O)_6^{3+}$ or $Cr(H_2O)_4Cl_2^{+}$ are impregnated into silica gel and nitric acid or hydrochloric acid is removed (Table II and the section, Reactions of Cr(III) on Silica), polymer results. This reaction is analogous to the similar formation of high polymer in solution by olation.[23] The rate of decomposition of $Cr(NH_3)_6^{3+}$ ion-exchanged onto silica is substantially augmented by removal of pore water. The visible spectrum of a partially decomposed sample (Figure 2) shows the presence of unreacted hexaammine and of polymer and the absence of detectable amounts of chromium(III) aquoammines. Thus, the hexaammine reacts with water in the hydrogen-bonded layer to liberate ammonia and all intermediates hydrolyze rapidly compared with the original hexaammine. Intermediate aquoammines are acidic enough to effect the conversion of $\equiv SiO^-$ to $\equiv SiOH$. The resulting formation of hydroxoammines, for example, $Cr(NH_3)_5OH^{2+}$, may account in part for the more rapid reaction of the intermediates. That such hydroxo complexes tend to undergo condensation with the formation of polymer accords with the well-known behavior of aquo complexes of Cr(III). However, the occurrence of condensation polymerization requires these species to be mobile on the surface of silica under the conditions of our experiments. This mobility would be favored by conversion of $\equiv SiO^-$ to $=SiOH$ and of $Cr(H_2O)_6^{3+}$ to $Cr(H_2O)_3(OH)_3$.

Removal of pore water increases the rate of decomposition of $Cr(NH_3)_6^{3+}$ probably by reducing the solvation of surface $\equiv SiO^-$. The lowered solvation should augment the basicity of $\equiv SiO^-$ in the same way as removal of water from sulfolane greatly augments the basicity of the hydroxide ion.[24] However, a study of the effect of desiccation upon the color of indicators gave no evidence for any marked increase in the H_- function of the surface, but we could not examine the proper function, H_{++}. Thus, the possibility that removal of the pore water augments the rate *via* increase in basicity of SiO^- in the reaction

$$Cr(NH_3)_6^{3+} + \equiv SiO^- = Cr(NH_3)_5NH_2^{2+} + \equiv SiOH$$

remains problematic. Alternatively, the removal of pore water may act by increasing the nucleophilic character of $\equiv SiO^-$ in the following reaction which must be considered nearly irreversible.

$$Cr(NH_3)_6^{3+} + \equiv SiO^- = \equiv SiO\text{-}Cr(NH_3)_5^{2+} + NH_3$$

Conversion of the purple to the final green stage of the gel can be effected by protracted desiccation at room temperature or by a short period of heating at 110°. The chemical differences between the green stage prepared as just described and the purple stage appear to be small. The spectra differ mainly in that the ratio of the extinction coefficient of the band at 4250 Å to that at ~5900 Å is unity in the green gel but less than unity in the purple gel as shown in Figure 2c. The epr spectra of the green and purple gels are similar and like Figure 3a.

Unlike the optical absorption spectra, the epr spectra show that partially decomposed hexaammine gel contains at least one species in addition to undecomposed hexaammine and polymer. The species is characterized by two epr absorptions at low fields, and it persists into the purple and green stages (see Figure 3a). However, heating freshly prepared hexaammine gel at 140° in air gives a green gel from which the two low-field absorptions have disappeared and in which the symmetry of the polymer band has increased (Figure 3b). The epr spectrum is now very similar to that of polymer deposited on silica (Figure 3c). During this heating of fresh gel at 140°, substantial amounts of Cr(VI)

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[19] A. Nicula, D. Stamires, and J. Turkevich, *J. Chem. Phys.*, **42**, 3684 (1965).

[20] J. H. de Boer, M. E. A. Hermans, and J. M. Vleeskens, *Konink. Ned. Akad. Wetenschap., Proc.*, **60B**, 45, 54 (1957).

[21] R. K. Iler, "The Colloid Chemistry of Silica and Silicates," Cornell University Press, Ithaca, N. Y., 1955.

[22] We found the water content of a gel after desiccation at 20°, 10^{-2} torr, to be 0.064 g/g of silica gel. A monolayer would amount to 0.051 g, assuming that a water molecule covered 20 Å^2.

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are formed. However, aging the gel at room temperatures for a week before heating leads to less Cr(VI).

The transition from the purple to the green stage seems to result just from further condensation in the polymer initially formed. Since exposure of the green gel to 0.1 *M* nitric acid at room temperatures results in no color change, the condensation process is not readily reversible. However, at near 100°, the green gel turns purple and Cr(III) is slowly extracted into solution.

We suggest that the low-field lines arise from isolated Cr(III) (or possibly dimers of Cr(III)), that these ions are readily oxidized to Cr(VI) at 140°, and that they are unstable *vs.* polymer. The isolated ions may be somewhat immobilized by entrance of $\equiv SiO^-$ into the coordination sphere to form $\equiv SiOCr(H_2O)_5{}^{2+}$, but any such species is clearly much less readily formed than the Co(III) analog.[6] Oxidation of isolated Cr(III) does not give Cr(V). Since Cr(V) is formed during oxidation at 250°, it probably results from oxidation of polymer. However, we cannot completely exclude the possibility that it originates from decomposition of Cr(VI) at these temperatures.

Somewhat similar low-field lines observed with chromia–alumina have been assigned to isolated Cr(III) ions surrounded by six oxide ions in an axially distorted octahedron.[1]

Oxidation of Cr(II) Ions on Silica. As just described, isolated ions of Cr(III) are oxidized to Cr(VI) at 140° and polymer is oxidized at 250° to Cr(VI) accompanied by rather large amounts of Cr(V). As judged by its optical absorption spectrum, the Cr(VI) is polymerized. Cr(II), as one might expect, is much more readily oxidized than Cr(III).

In the absence of air, Cr(II) deposited by ion exchange with $Cr(H_2O)_6{}^{2+}$ is stable when the pores are largely filled with water; that is, its stability is like that in solution. Since this ion is coordinatively labile, there may be some entrance of the $\equiv SiO^-$ group into the coordination sphere,[6] but we have no evidence on this matter. On the other hand, Cr(II) made by reduction of Cr(III) by carbon monoxide at 450° is oxidized by water vapor.[2] The precise coordination of Cr(II) in the second case is unknown, but in view of its history it is not a simple hydrated ion and it is probably coordinatively unsaturated.[2] This must account for its oxidizability by water.

Oxygen is a two- or a four-electron oxidizing agent accordingly as it forms $O_2{}^{2-}$ or $2O^{2-}$. Thus, it cannot oxidize Cr(II) to Cr(III) in any simple process. In solution, it appears that the following process occurs.[25,26]

$$\mathrm{Cr(II)} = \mathrm{Cr(IV)} + 2e$$

$$\mathrm{Cr(IV)} + \mathrm{Cr(II)} = \text{dimeric Cr(III)}$$

The Cr(IV) species has been formulated as $Cr(O\text{–}O)^{2+}$. No Cr(VI) is formed during oxidation of Cr^{2+} in solution at room temperatures. In oxidizing adsorbed Cr(II), the second step of the reaction in solution might be hindered and particularly so in gel prepared by reduction of Cr(III) at high temperatures.

Indeed, oxidation at room temperatures of the $Cr(H_2O)_6{}^{2+}$ gel (after removal of free pore water) or of the reduced Cr(III) gel does give Cr(VI) and a few per cent Cr(V) as well as Cr(III). At −78° oxidation is still very rapid. After warming the oxidized gel to room temperatures, the epr shows a little Cr(V) but no detectable Cr(III); one may extract some Cr(VI).

If $Cr(O\text{–}O)^{2+}$ is the first product of reaction of oxygen with Cr(II), then in that fraction of $Cr(O\text{–}O)^{2+}$ which is prevented by isolation and immobility from reacting with Cr(II), the peroxy unit may further oxidize $Cr^{(IV)}\text{-}(O\text{–}O)^{2+}$ to Cr(VI). Over-all, the oxygen molecule would then act as a four-electron oxidizing agent.

Considering the low precision of quantitative analysis by epr, we obtain a reasonable material balance for the distribution of chromium among Cr(III), Cr(V), and Cr(VI) after oxidation at 20° but, at −78°, most of the content in the chromium is undetected. The missing chromium may be Cr(IV) but, if so, why some reacts further to Cr(VI) and some does not is unclear.

Although our experiments dealing with the oxidation of Cr(II) are not extensive, they do provide a striking example of an important aspect of surface chemistry: hindrance to mobility of surface species with the resulting suppression of reactions between species which occur readily in solution.

Cr(V). The determination of the exact geometry of the surface species which give the various Cr(V) signals is a complicated matter which depends upon the coordination number of Cr(V), its geometry, the identity of the ligands, and, possibly, environmental factors. Indeed, one group assigns the signal not to Cr(V) but to an exchange coupling between Cr(III) and Cr(VI).[27] In the more conventional interpretation,[28] our Cr(V) signals result from pentacoordinate square-pyramidal species or tetrahedral species of low local symmetry. Other tetrahedral species should give detectable signals only at very low temperatures. The values of $g_\perp$ and $g_\parallel$ which we measured at 22° for a sample of hexaammine gel heated in oxygen at 250° and then exposed to air at 22° are almost identical with those reported[28] for a silica impregnated with an aqueous solution of CrO_3 which had been calcined at 500° and exposed to water vapor at 20°. This signal was assigned to a square-pyramidal species.

We have observed a rather large number of different Cr(V) signals at 22° of which only three are shown in Figure 5. There must be a rather large number of different species of Cr(V) which we shall not attempt further to characterize at this time.

Acknowledgement. One of us (D. C.) received a grant from NATO while on leave from the University of Caen. We are indebted to Dr. Jerome A. Roth for determining the epr spectra of gels impregnated with hexaammine and to Mr. L. J. Schmauch of the American Oil Co., Whiting, Ind., for determining the molecular weight of chromia polymer by ultracentrifugation. This work was supported by the Petroleum Research Fund of the American Chemical Society, Grant 1579-C.

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