542. *The Oxidation of Chromous Perchlorate with Sodium Azide.*

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The oxidation of chromous perchlorate with sodium azide in aqueous perchloric acid yielded three complex ions: hexa-aquochromium(III), penta-aquomonoamminechromium(III), and a binuclear chromium(III) ammine. This complex, believed to have the structure $(H_2O)_5Cr{-}NH{-}Cr(H_2O)_5{}^{4+}$, was isolated as the sulphate. The presence of chloride ion affects the nature of the products. A reaction mechanism is suggested.

The composition of the chromic complexes produced by the oxidation of an acidified chromous perchlorate solution depends on the nature of the oxidizing agent. They are highly aquated, in most cases containing five water molecules co-ordinated with the chromic ion. Complex ions of the type $Cr^{III}(H_2O)_5X$ ($X = Cl^-, F^-, Br^-, I^-, SO_4{}^{2-}, N_3{}^-, CNS^-$, etc.) are formed by oxidation with $Co^{III}(NH_3)_5X$ or X_2.[1] Another group of oxidizing agents yields the binuclear chromic ion[2] $Cr_2O_{aq}{}^{4+}$. Many compounds containing nitrogen are reduced by acidified chromous perchlorate solutions. These reactions often proceed stepwise, producing intermediate complexes such as $Cr(H_2O)_5NO^{2+}$,[3] but the final product is usually the free ammonium ion.

The reduction of azide by chromous solutions was investigated by Traube and Lange.[4] They found that two chromous ions are consumed by each azide ion (or hydrazoic acid molecule), leading to the production of one nitrogen molecule and one ammonia molecule:

$$2Cr^{2+} + 2H^+ + HN_3 \longrightarrow Cr^{3+} + NH_3 + N_2$$

We confirmed this result, but observed that the ammonia produced in the reaction is co-ordinated with the chromic ion. The chromic complexes produced in the reaction were separated by ion-exchange chromatography, and two chromium ammines were isolated: the penta-aquomonoamminechromium(III) and a binuclear chromium(III) monoammine.

Experimental

Materials.—Chromic and chromous perchlorate were prepared as described previously.[2] The acidified solution of chromous perchlorate (~0·6M) was kept under nitrogen in a gravity-type storage burette.[5]

Analysis.—Chromium was determined spectrophotometrically as the chromate at 372 mμ after oxidation with alkaline hydrogen peroxide.[2] Ammonia was determined by the Kjeldahl method, and sulphate as barium sulphate. The absorption spectra were measured with a Beckman B spectrophotometer.

The Oxidation.—Chromous perchlorate (2 mmoles) was added to sodium azide (65 mg.; 1 mmole) dissolved in 0·1N-perchloric acid (100 ml.). In some experiments, 10 ml. of 1N-perchloric acid were used. All solutions were oxygen-free. After 10 min. the solution was vigorously shaken, in order to expel the nitrogen bubbles formed during the reaction, and absorbed on the ion-exchange column.

Separation of the Products.—The solution containing the reaction products was passed through a cation-exchange column (1 cm.² cross section and 10 cm. in height) containing a Zeo-Karb 225 cation-exchange resin (H⁺ form; 52—100 mesh, 2% of divinylbenzene). The chromic species were absorbed in three bands, the uppermost red-violet, the middle violet, and the lowest grey-blue. Perchloric acid was used as an eluant. Both the lowest and the middle band were eluted with 1N-acid and the highest band with 2N-acid. The separation between the first two fractions was not complete (both are tripositive ions). By use of a resin with higher cross-linking (Dowex 50; 8% of divinylbenzene), complete separation was achieved. The absorption spectrum of each fraction was taken: the grey-blue fraction had $\lambda_{max.}$ 408

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[1] Taube, *Adv. Inorg. Chem. Radiochem.*, 1959, **1**, ch. I.

[2] Ardon and Plane, *J. Amer. Chem. Soc.*, 1959, **81**, 3197; Ardon and Linenberg, *J. Phys. Chem.*, 1961, **65**, 1443.

[3] Ardon and Herman, *J.*, 1962, 507.

[4] Traube and Lange, *Chem. Zentr.*, 1926, 1, 1358.

[5] Stone, *Analyt. Chem.*, 1948, **20**, 747.

(ε 15·8) and 574 mμ (ε 13·4). It was identified as the hexa-aquochromic ion. The middle fraction had maxima at 397 (ε 21·8) and 545 mμ (ε 22·1). The highest fraction had maxima at 407 (ε 24·5) and 547 mμ (ε 16·7). In some experiments a small amount of the azidopenta-aquochromic ion was found in the solution—it formed a narrow green band below the hexa-aquo-band and was easily eluted with 0·5N-perchloric acid.

When perchloric acid was replaced by hydrochloric acid before the oxidation, different products were obtained: in this case the two complexes, $Cr(H_2O)_5Cl^{2+}$, and the violet complex (identical with the middle fraction mentioned above) were the only products. They were separated by elution with 0·5N-perchloric acid which easily eluted the green chloro-complex, followed by 1N-acid for elution of the violet complex. Notably, these two complexes were formed in equal amounts in all the experiments in hydrochloric acid solution.

Isolation of the Chromium Ammines.—The middle fraction, containing the violet complex in 1N-perchloric acid, was absorbed on a small column (0·5 cm.^{2} cross section and 3 cm. in height) containing the Zeo-Karb resin (H^+ form, 2% of divinylbenzene); after being washed with water it was eluted with 2N-sulphuric acid The *sulphate* was precipitated from the resulting concentrated solution by ethanol, filtered off, washed with ethanol, and dried with ether {Found: Cr, 17·1; N, 4·6; SO_4, 47·3. $[CrNH_3(H_2O)_5]_2(SO_4)_3$ requires Cr, 17·2; N, 4·6; SO_4, 47·5%}.

The binuclear chromium amine ion (highest fraction) was isolated as red-violet crystals in a similar way from the third fraction {Found: Cr, 21·8; N, 2·80; SO_4, 38·7. $[(H_2O)_5Cr{-}NH{-}Cr(H_2O)_5](SO_4)_2$ requires Cr, 21·2; N, 2·85; SO_4, 39·1%}.

DISCUSSION

The existence of a stable penta-aquomonoamminechromium ion was doubted [6] until Jørgensen and Bjerrum [7] proved that it is formed as an intermediate in the aquation of the tetra-aquodiamminechromium ion. They separated this ion from the diammine and the hexa-aquochromium and measured its absorption spectrum, but could not isolate it as a salt of definite composition. The absorption spectrum is similar to that of our middle fraction which was shown by analysis to be the monoammine and was isolated as the sulphate, $[(CrNH_3(H_2O)_5]_2(SO_4)_3$.

The highest fraction was shown to contain chromium and nitrogen in the ratio 2 : 1. The charge is 2+ per chromium atom (from analysis of the sulphate). From its behaviour on the ion-exchange column it is evident that the total charge of the complex ion is higher than 3+. A binuclear tetrapositive structure is therefore almost certain. Of the various binuclear tetrapositive structures, we believe that the most probable is $(H_2O)_5Cr{-}NH{-}Cr(H_2O)_5{}^{4+}$, but other structures could also account for the experimental data, *e.g.*, the ion $(NH_3)(H_2O)_4Cr{-}O{-}Cr(H_2O)_5{}^{4+}$ which has an oxygen bridge between the two chromium atoms.

The specific effect of the chloride ion on the reaction products gives a clue to the mechanism of the reaction. It is suggested that in the absence of chloride ions (oxidation in perchloric acid solution) the reaction proceeds by two competing paths:

$$2Cr^{2+} + HN_3 + 2H^+ \begin{array}{l} \nearrow CrNH_3(H_2O)_5{}^{3+} + Cr(H_2O)_6{}^{3+} + N_2 \\ \searrow (H_2O)_5Cr{-}NH{-}Cr(H_2O)_5{}^{4+} + N_2 + 2H^+ \end{array}$$

thus leading to the three chromic complexes. The chloride ion, which is an efficient catalyst in many redox reactions,[1] is assumed to accelerate the first path by a bridging mechanism which will produce the chloro-complex and the monoammine:

$$2Cr^{2+} + Cl^- + HN_3 + 2H^+ \longrightarrow Cr(H_2O)_5Cl^{2+} + CrNH_3(H_2O)_5{}^{3+} + N_2$$

This will explain the absence of the hexa-aquo and the binuclear ions, and the fact that the chloro-complex and the monoammine are formed in equal amounts, as found experimentally.

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[6] Remy, " Treatise on Inorganic Chemistry," Vol. II, Elsevier, Amsterdam, 1956, p. 146.

[7] Jørgensen and Bjerrum, *Acta Chem. Scand.*, 1958, **12**, 1047.