95. *The Complex Ion* $Cr(H_2O)_5NO^{2+}$.

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The oxidation of Cr^{II} by nitrate or nitric oxide produces three chromic complexes which have been separated by ion-exchange chromatography. One of them was shown to have the composition $Cr(H_2O)_5NO^{2+}X^-{}_2$ and was isolated as the sulphate. The mechanism of the oxidation is discussed.

Recently it was observed that when chromous ions were oxidised by nitrate the mixture became reddish-brown. As this colour was not observed with other oxidising agents, it pointed to the formation of a chromic complex containing nitrogen. Later we found that when nitric oxide was used as oxidising agent in place of nitrate the red-brown colour was much more intense.

Chesneau,[1] who investigated this reaction, passed nitric oxide through a solution of chromous chloride and found the ratio of the absorbed nitric oxide to chromium to be 1 : 3 and so was misled into suggesting that the reddish-brown compound was a chromous complex $(CrCl_2)_3NO$. Kohlschütter,[2] investigating the same reaction, concluded that the chromous ion was oxidised to the chromic state, while the nitric oxide was reduced to hydroxylamine or to ammonia depending on the acidity of the solution. The nature of the red-brown compound remained unknown.

Taube and Myers [3] observed that the oxidation of chromium(II) in acid solution often produces a mixture of $Cr(H_2O)_6{}^{3+}$ and its substitution products $Cr(H_2O)_5X^{2+}$, and it was later observed [4] that in many oxidations a dinuclear, tetrapositive green ion Cr_2O^{4+} is also formed.

The oxidation of chromium(II) by nitrate or by nitric oxide produces, not one, but three chromic complexes, all of which are extremely soluble. This is, apparently, why early attempts to determine the nature and composition of the red-brown solution have failed.

Cation-exchange resins were first employed by Gustavson [5] for the separation of chromic complexes in basic chrome tanning liquors. King and his co-workers [6] achieved, by the same technique, such delicate separations as the resolution of *cis–trans*-isomers of the type $Cr(H_2O)_4X_2{}^+$, and Laswick and Plane [7] elucidated the nature of boiled chromic salt

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[1] Chesneau, *Comp. rend.*, 1899, **129**, 100.

[2] Kohlschütter, *Ber.*, 1904, **37**, 3053; cf. Remy, "Treatise on Inorganic Chemistry," Elsevier, Amsterdam, 1956, Vol. II, p. 133.

[3] Taube and Myers, *J. Amer. Chem. Soc.*, 1954, **76**, 2103.

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

[5] Gustavson, *Svensk Kem. Tidskr.*, 1944, **56**, 14.

[6] Hougen, Schug, and King, *J. Amer. Chem. Soc.*, 1957, **79**, 519; King, Woods, O. P. Gates, and H. S. Gates, *ibid.*, 1958, **80**, 5015.

[7] Laswick and Plane, *J. Amer. Chem. Soc.*, 1959, **81**, 3564.

solutions by ion-exchange chromatography. By a similar technique, we separated the red-brown solution produced by the oxidation of chromium(II) with nitric oxide or nitrate into the dinuclear, green ion Cr_2O^{4+}, the hexaquochromic ion $Cr(H_2O)_6^{3+}$, and a new complex $Cr(H_2O)_5NO^{2+}$, having a deep red-brown colour, which is responsible for the colour of the solution.

EXPERIMENTAL

Materials.—Chromic and chromous perchlorate were prepared as described previously.[4] Other chemicals were of "AnalaR" grade.

The Oxidation.—A burette containing chromous perchlorate under nitrogen was dipped under the surface of water or dilute perchloric acid (100 ml.) in a 125 ml. flask. Oxygen was expelled with purified nitrogen, then purified nitric oxide (Matheson) was bubbled through the solution and acidified; ~0·6M-chromous perchlorate (4—6 ml.) was added slowly with stirring. Nitrogen was then bubbled through the solution to expel the excess of nitric oxide.

Analysis.—Chromium was determined volumetrically, after oxidation with persulphate, by titration with ferrous sulphate or spectrophotometrically[8] as the chromate at 372 mμ after oxidation with alkaline hydrogen peroxide. The nitrogen content was determined by the Kjeldahl method after oxidation to nitrate with alkaline hydrogen peroxide and reduction with Devarda's alloy. In this way decomposition of the complex with consequent loss of nitric oxides was avoided.

The degree of oxidation of the nitric ligand was determined as follows: an excess of standardized ceric perchlorate in 6M-perchloric acid was added to the complex, dilute sulphuric acid was added, and the solution titrated with ferrous sulphate.

Sulphate was determined as barium sulphate.

The absorption spectra were measured with an Optica Milano CF4 spectrophotometer.

Separation of the Products.—Chromous perchlorate was oxidised by nitric oxide or nitric acid and the resulting solution was passed through a cation-exchange column (1 cm.^{2} cross-section, 10 cm. in height) containing Zeo-Karb 225 resin (H^+ form; 50—100 mesh). The chromic species were absorbed in three bands, uppermost green, the middle grey-blue, and the lowest deep red-brown. The red-brown band was eluted with 0·2M-perchloric acid. The grey blue band was eluted with 0·5M-perchloric acid and was identified as containing $Cr(H_2O)_6^{3+}$. The green band was eluted with 2M-perchloric acid and was identified as containing the dinuclear Cr_2O^{4+}. The use of this resin of low cross-linking (2%) permitted elution of the highly charged ions with hydrogen ions, and thereby the use of heavy-metal ions was avoided. The absorption spectrum of $Cr(H_2O)_5NO^{2+}$ from the lowest band, measured in 0·1M-perchloric acid, had maxima at 323 (ε 92), 449 (ε 120), and 559 mμ (ε 28).

The proportions of the three complexes formed depended on the conditions of the oxidation: when nitric oxide was used the yield of the nitric oxide complex reached 40% in some experiments, but with nitric acid was much lower. In a typical experiment in which 0·15M-nitric acid was used as oxidant, the ratio $CrNO^{2+} : Cr^{3+} : Cr_2O^{4+}$ was 1 : 2·26 : 1·13. When nitric oxide was used in neutral aqueous solution, the ratio was 1 : 0·95 : 0·38, and when the same reaction was carried out in 0·5M-perchloric acid the ratio was 1 : 0·84 : 0·25. Decreasing the rate of inflow of chromous salt and increasing the rate of stirring increased the yield of $CrNO^{2+}$ complex.

Preparation of the Sulphate $[Cr(H_2O)_5NO]SO_4$.—10 Millimoles of oxidised chromium were absorbed on a larger column (10 cm.^{2} in cross-section and 10 cm. in height) and the $CrNO^{2+}$ was eluted with 0·7N-sulphuric acid. The concentrated solution of the nitric oxide complex was placed in a vacuum desiccator over sodium hydroxide. After 24 hr. the red-brown crystals that were formed were separated by decantation, washed with ethanol, air-dried, and kept in a desiccator. They are stable for months in a dry atmosphere but their aqueous solution slowly decomposes owing to aquation.

The oxidation number of the nitric oxide ligand in this *sulphate* {Found: Cr, 19·2; N, 5·2; SO_4, 35·9. $[Cr(H_2O)_5NO]SO_4$ requires Cr, 19·4; N, 5·2; SO_4, 35·8%} was determined by oxidation with ceric perchlorate and titration with ferrous sulphate. The ligand is oxidised to nitrate (+5) and it was found that four equivalents of cerium(IV) were consumed for each nitrogen atom. The oxidation of chromium(III) to chromium(VI) by the same reagent does not

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[8] Haupt, *J. Res. Nat. Bur. Standards*, 1952, **48**, 414.

affect the result, because the latter is reduced by ferrous ion just as is cerium(IV), while the nitrate is not. It was thus shown that the nitrogen in the complex has the oxidation number +1, and the ligand is therefore NO^- (provided the chromium is in the tervalent state).

DISCUSSION

The only known monosubstituted aquo-complex of the type $M(H_2O)_5NO^{n+}$ is the "brown ring" compound $Fe(H_2O)_5NO^{2+}$. The nitrosopenta-aquochromic ion is probably a true nitroso-complex containing the NO^- group, whereas the ferrous compound is a nitrosyl compound containing the NO^+ group.[9]

This complex is probably formed directly by the reaction $Cr^{2+} + NO \longrightarrow CrNO^{2+}$. The fact that it is obtained (in lower yield) by oxidation with nitrate is attributed to the fact that nitrate, like chlorate, is reduced in steps.[10] Some of those steps involve two-electron transfer (oxygen atom transfer) and produce Cr_2O^{4+} (cf. ref. 4), and some proceed by one-electron transfer and produce $Cr(H_2O)_6^{3+}$. When the reduction reaches the nitric oxide stage, the red-brown complex is formed by interaction with chromium(II). Although the yield of the complex is much higher when nitric oxide is used it is usually less than 50% of the total chromium because the NO^- group is further reduced by chromium(II) to hydroxylamine or ammonia.[1,2] The complex competes with the nitric oxide in the oxidation of chromium(II). Therefore the highest yield of the complex is obtained when using an excess of nitric acid and a high rate of stirring, which lowers the local excess of the complex. The yield is increased also by increasing the volume of the reacting solution, which decreases the concentration of the complex in the bulk of the solution without affecting the concentration of the nitric oxide.

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[9] Griffith, Lewis, and Wilkinson, *J.*, 1958, 3993.

[10] Halperin and Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 35, 380.