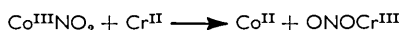


**668. Reductions by Chromium(II) of Cobalt(III) Complexes containing Oxyanions of Nitrogen**

By R. T. M. FRASER

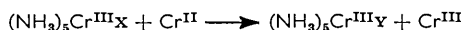
The reduction by chromium(II) of penta-aminocobalt(III) complexes containing  $(\text{NO})_2$  and  $\text{NO}_2$  ligands has been re-investigated. In all cases the first step is the reduction of the cobalt(III) centre.

RECENTLY it was suggested<sup>1</sup> that the reaction of chromium(II) with penta-aminocobalt(III) complexes containing nitrogen oxyanions involves the reduction of the ligand to  $\text{NO}^-$  before co-ordination to the chromium ion. If this is true, the reactions would constitute an important new class of reductions by chromium(II), for the usual bridging mechanism presupposes that the ligand becomes firmly bound to chromium(III) in the first electron-transfer process: for example, in the reduction of nitropenta-aminocobalt(III), the mechanism normally suggested would include

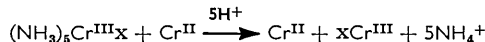


as a step preceding the ligand reduction which yields finally  $[(\text{H}_2\text{O})_5\text{CrNO}]^{2+}$ . In the hope of providing further evidence for the new type of reaction, a more detailed study has been made of the reduction of chromium(III) and cobalt(III) complexes containing the hyponitrito-, nitro-, and nitro-ligands ( $-\text{O}-\text{N}=\text{N}-\text{O}-$ ,  $-\text{NO}_2$ , and  $-\text{O}-\text{N}=\text{O}$ , respectively).

With chromium(III) complexes, it can be established very easily whether reduction of the cobalt or of the ligand occurs first, for the kinetics will be second-order if the first step involves the ligand,



but pseudo-first-order if the electron transfer is to the metal,



In the second case, the rate constant will not depend on the initial concentration of the complex, even when this is greater than that of the chromium(II) ion, or

$$-d[\text{Cr}^{\text{II}}]/dt = k[\text{Cr}^{\text{III}}] = k'[\text{Cr}^{\text{II}}][\text{Cr}^{\text{III}}].$$

Behaviour corresponding to the latter is found: at  $25^\circ$ , the rate constant observed for the reduction of nitropenta-aminocobalt(III) ion is  $0.27 \text{ sec}^{-1}$  in the ranges  $0.2\text{--}0.6\text{M}$ -perchloric acid and  $1.0\text{--}3.0 \times 10^{-3}\text{M}$ -complex ( $[\text{Cr}^{\text{II}}]_0 = 1.0 \times 10^{-3}\text{M}$ ) and  $0.14 \text{ sec}^{-1}$  ( $[\text{Cr}^{\text{II}}]_0 = 0.5 \times 10^{-3}\text{M}$ ), yielding a second-order rate-constant of  $275 \text{ moles}^{-1} \text{ sec}^{-1}$ . The pseudo-first-order kinetics slowly change to second-order as the concentration of the reduced species increases. A total of three equivalents of chromium(II) are required to convert the nitrito-complex into the nitrosyl: two of these are added, the third is generated from the complex as the reaction proceeds.

Three equivalents of reductant are also required for the formation of one chromium nitrosyl from nitrito- or nitro-penta-aminocobalt(III). At  $25^\circ$ , and an ionic strength of  $0.2$ , the amount of nitrito-complex converted into cobalt(II) is  $53\%$  after the addition of the first equivalent of chromium(II),  $80\%$  after the second, and  $100\%$  after the third. At an ionic strength of one (the strength at which the kinetic measurements were made), the values were  $96$ ,  $99$ , and  $100\%$ , respectively. The corresponding values in the reduction of the nitro-complex were  $64$ ,  $87$ , and  $99\%$ , and  $97$ ,  $99$ , and  $100\%$ . It was not possible to determine the specific rate for either of the cobalt(III) reductions, as was done for the chromium(III), because the reactions were too fast. The speed of the first step does allow the second and third stages to be treated independently as a bimolecular-bimolecular pair,

<sup>1</sup> W. P. Griffith, *J.*, 1963, 3286.

and the method of Wells<sup>2</sup> was used to obtain the ratio of the specific rates. The ratios used in the evaluation are shown in the Table.

Specific rate ratios for the reduction of penta-aminecobalt(III) complexes

Complex	[H <sup>+</sup> ] (M)	[D] <sub>t</sub> /[A] <sub>0</sub> *	k <sub>3</sub> /k <sub>2</sub>	Complex	[H <sup>+</sup> ] (M)	[D] <sub>t</sub> /[A] <sub>0</sub> *	k <sub>3</sub> /k <sub>2</sub>
Nitro .....	0.2	0.114	0.10	Nitrito .....	0.2	0.33 <sub>5</sub>	1.4
„ .....	0.4	0.24	0.46	„ .....	0.4	0.38	2.0
„ .....	0.6	0.32	0.88	„ .....	0.6	0.40	2.4

\* Fraction of chromium nitrosyl formed after the addition of the second equivalent of chromium(II).

Ligand reduction is not involved in the reaction of  $\mu$ -hyponitrito-bis[penta-aminecobalt(III)], and two equivalents of chromium(II) give rise to two equivalents of the chromium nitrosyl. It was found that, on addition of the first equivalent, the reduction of the complex

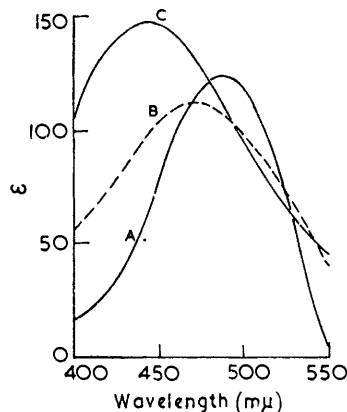
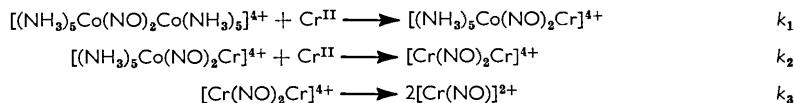


FIGURE 1. Absorption change in the reaction of chromium(II) and  $\mu$ -hyponitrito-bis[pentamminecobalt(III)]:

A,  $\mu$ -hyponitrito-bis[pentamminecobalt(III)] ([H<sup>+</sup>] = 0.6M).  
B, after addition of one equivalent of Cr(II).  
C, after addition of one further equivalent of Cr(II)

follows second-order kinetics for 85–95% of the reaction, suggesting that the reduction of the first cobalt centre is much more rapid than that of the second. Accordingly, the mechanism suggested is



The molecular extinction curves for the three ions are shown in Figure 1. If  $k_1$  is very much greater than  $k_2$  or  $k_3$ , the second and third steps may be treated as a bimolecular-unimolecular pair of consecutive reactions. If  $[\text{Cr}^{\text{II}}]_0 = [(\text{NH}_3)_5\text{Co}(\text{NO})_2\text{Cr}]^{4+}_0$  the concentration of the nitrosyl at time  $t$ , is given by<sup>3</sup>

$$[\{\text{Cr}(\text{NO})\}^{2+}]_t = a[1 - e^{-\kappa(\tau-1)} - \kappa e^{-\kappa\tau}D] \quad (1)$$

where  $a = [(\text{NH}_3)_5\text{Co}(\text{NO})_2\text{Cr}]^{4+}_0$ ,  $\tau = 1 + ak_2t$ ,  $\kappa = k_3/k_2a$ , and  $D$  is the difference of the exponential integrals,<sup>4</sup>  $E_1(\kappa\tau) - E_1(\kappa)$ . A method of successive approximations was used to evaluate  $k_2$  and  $k_3$ . Values of  $[\{\text{Cr}(\text{NO})\}^{2+}]_{100}/a$  were calculated from equation (1) by replacing  $ak_2 = 0.1$  by various values of  $\kappa$ . Figure 2 shows the calculated curve, together with curves for  $ak_2 = 0.01, 0.02, 0.04$ , and  $0.07$ . Similar families of curves were calculated for  $[\{\text{Cr}(\text{NO})\}^{2+}]_{200}/a$  and  $[\{\text{Cr}(\text{NO})\}^{2+}]_{400}/a$ . A comparison of the experimental value of  $[\{\text{Cr}(\text{NO})\}^{2+}]_{100}/a$  with the calculated curves gave pairs of  $\kappa$  and  $ak_2$  values satisfying the kinetic requirements, and a plot of  $\kappa$  vs.  $ak_2$  was made. The process was repeated for  $t = 200$  and  $t = 400$ , and the point of intersection of the three curves gave the values of  $k_2$  and  $k_3$  for the reaction. At 20°, the first values obtained were  $k_1 = 545 \text{ moles}^{-1} \text{ sec}^{-1}$ ,

<sup>2</sup> P. R. Wells, *J. Phys. Chem.*, 1959, **63**, 1978.

<sup>3</sup> J. Chien, *J. Amer. Chem. Soc.*, 1948, **70**, 2256.

<sup>4</sup> E. Jahke and F. Emde, "Tables of Functions," ed. B. G. Teubner, Leipzig, 1933, p. 83.

$k_2 = 51 \text{ moles}^{-1} \text{ sec.}^{-1}$ , and  $k_3 = 5.0 \times 10^{-3} \text{ sec.}^{-1}$ . It is clear that  $k_2$  is so large compared to  $k_1$  that a correction must be applied for the amount of  $[\text{Cr}(\text{NO})_2\text{Cr}]^{4+}$  formed before the second equivalent of chromium(II) is added. The correction can be derived from the values of Wells.<sup>2</sup> In this particular case,  $k_2/k_1 = 0.094$ , so that  $[\{\text{Cr}(\text{NO})\}^{2+}]/a = 0.11$ . The observed concentrations of  $\text{Cr}(\text{NO})^{2+}$  were corrected for this, and the entire procedure repeated until constant values for  $k_2$  and  $k_3$  were obtained. Figure 3 shows the experimental values of  $[\{\text{Cr}(\text{NO})\}^{2+}]/a$ , together with the calculated curve for  $k_2 = 76 \text{ moles}^{-1} \text{ sec.}^{-1}$  and  $k_3 = 3.2 \times 10^{-3} \text{ sec.}^{-1}$ . At  $15^\circ$ ,  $k_1$  is  $410 \text{ moles}^{-1} \text{ sec.}^{-1}$  and  $k_2$  is  $55 \text{ moles}^{-1} \text{ sec.}^{-1}$ : the rate constant  $k_3$  shows little change.

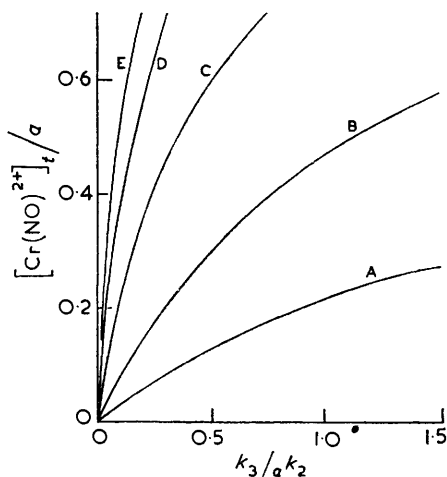


FIGURE 2. Yield of chromium nitrosyl;  $ak_2t = 1$  (A), 2 (B), 4 (C), 7 (D), and 10 (E);  $a = [\{\text{NH}_3\}_5\text{Co}(\text{NO})_2\text{G}\}^{4+}]_0$

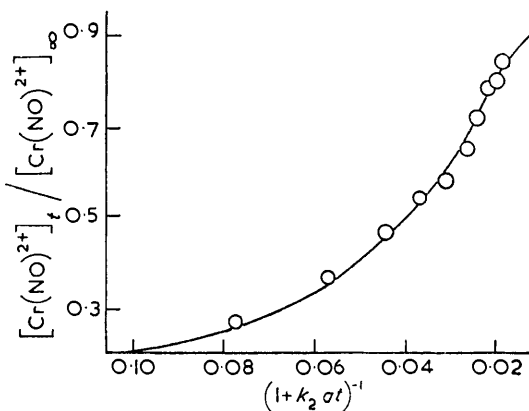
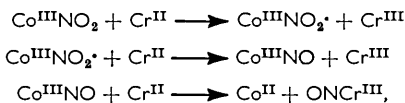


FIGURE 3. Yield of chromium nitrosyl at  $20^\circ$ ; (O) experimental values, (—) calculated curve using  $k_2 = 76 \text{ moles}^{-1} \text{ sec.}^{-1}$ ,  $k_3 = 3.2 \times 10^{-3} \text{ sec.}^{-1}$

## DISCUSSION

It is true that the rates of reduction by chromium(II) of the ions used as ligands can be fast. However, it has been found<sup>5</sup> that the rates of reduction of the cobalt centre in pentaamminecobalt(III) complexes containing these ligands are even faster, so that all the ligands are transferred unchanged to the chromium. Exceptions to this can arise only when the site of ligand reduction lies outside the path of electron transfer leading to metal reduction. In such cases, the rate of reduction of the cobalt(III) and that of the ligand proceed independently; the *p*-nitrobenzoate complex is one example.

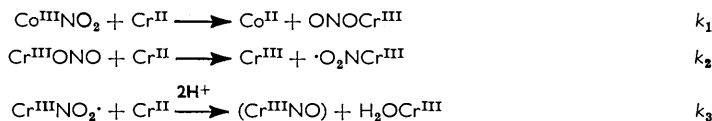
The results of the nitropenta-amminechromium(III) reaction show conclusively that ligand reduction takes place subsequently to reduction of the chromium(III). A similar demonstration is not possible with the cobalt(III) complexes, but the sequence of reactions can still be established with some certainty. If ligand reduction were the first step, the sequence would be



and the maximum amount of cobalt(II) that could be formed under any condition would be equal to one-third of the chromium(II) added. The experiments show, however, that much more than this is formed, even at low ionic strengths, so that reduction of cobalt(III) must be the first step in the reaction. The values of  $k_3/k_2$  obtained in the nitro-reduction

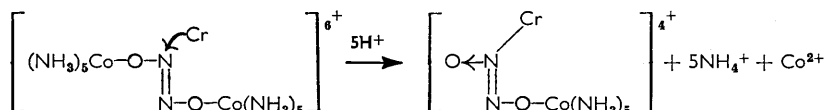
<sup>5</sup> E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, 1964, **86**, 1318.

suggest that two hydrogen ions more are involved in the third transition state than in the second: rewriting  $k_3$  as  $k_3''[H^+]^2$ , the ratio  $k_3''/k_2$  is 2.5 at 0.2M- $[H^+]$ , 2.9 at 0.4M, and 2.5 at 0.6M. The suggested reaction scheme is therefore

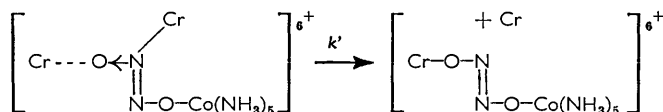


The specific ratios of the rates are not the same for the two reductions, but this is to be expected, since the chromium(II) can attack the nitro-complex at an oxygen only, but can attack the nitro-complex at either an oxygen or a nitrogen, to give rise to both  $[(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}\text{ONO}]^{2+}$  and  $[(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}\text{NO}_2]^{2+}$ .

The structure of the red cobalt nitrosyl now seems to be fairly well established. Conductivity studies on the nitrate show<sup>6</sup> it to be a one-four compound [that is, a dimer with the composition  $\text{Co}_2(\text{NH}_3)_{10}(\text{NO})_2(\text{NO}_3)_4$ ], and the infrared absorption of the NO group occurs at  $1050 \text{ cm}^{-1}$ , in good agreement with that found in hyponitrites.<sup>7</sup> The complex ion is therefore  $\mu$ -hyponitrito-bis[penta-aminecobalt(III)], with cobalt-oxygen bonding. An examination of a model of the ion suggests that reductant attack can take place only at the nitrogens, so that the first step in the reaction is



The formation of the 1 : 1 binuclear species will account for the slower rate of reduction on the addition of the second equivalent of Cr(II), for the nitrogen bonded penta-aquochromium(III) group introduces considerable steric hindrance. The alternative path,



need not be considered in the reaction scheme, because recent work<sup>8</sup> has shown that the rate of reduction through a ligand ( $-\text{N},\text{O}$ ) can be calculated if the rate for reduction through the isomeric ( $-\text{O},\text{N}$ ) is known: in this case, the rate constant  $k'$  would be small, lying in the range  $0.4\text{--}11 \text{ moles}^{-1} \text{ sec}^{-1}$  at  $20^\circ$ . The third step in the reaction is the fission of the  $\text{N}=\text{N}$  bond in  $[(\text{H}_2\text{O})_5\text{Cr}(\text{NO})_2\text{Cr}(\text{H}_2\text{O})_5]^{4+}$  to yield two chromium nitrosyl ions. {A distinction cannot be made in any of this work between  $[(\text{H}_2\text{O})_5\text{Cr}^{\text{I}}\text{NO}]^{2+}$  and  $[(\text{H}_2\text{O})_5\text{Cr}^{\text{III}}\text{NO}]^{2+}$ .}

#### EXPERIMENTAL

All reagents were of AnalaR quality. Nitropenta-aminechromium(III) perchlorate and nitropenta-aminecobalt(III) perchlorate were prepared as described by Linhard.<sup>9</sup> Nitropenta-aminecobalt(III) perchlorate was obtained from the isomerisation of the solid nitro-complex (room temperature, over a period of three months). The red  $\mu$ -hyponitro-bis[penta-aminecobalt(III)] perchlorate was prepared by Werner's method.<sup>10</sup> The solution of chromium(II) perchlorate was obtained from chromium(III) perchlorate by electrolytic reduction. The concentration of chromium(II) was determined by potentiometric titration with standard solutions of potassium permanganate or cerium(IV) sulphate. Solutions of the complexes in water were freshly made up by weight for each experiment. Initial concentrations were in the

<sup>6</sup> R. D. Feltham, *Inorg. Chem.*, 1964, **3**, 1038.

<sup>7</sup> L. Kuhn and E. R. Lippincott, *J. Amer. Chem. Soc.*, 1956, **78**, 1820.

<sup>8</sup> R. T. M. Fraser, *Inorg. Chem.*, 1964, **3**, 1561.

<sup>9</sup> M. Linhard, H. Siebert, and M. Weigel, *Z. anorg. Chem.*, 1955, **278**, 287.

<sup>10</sup> A. Werner and P. Karrer, *Helv. Chim. Acta*, 1918, **1**, 65.

range  $0.5\text{--}4.0 \times 10^{-3}\text{M}$ -complex and  $0.2\text{--}0.6\text{M}$ -perchloric acid. Sodium perchlorate was added to keep the ionic strength constant at 1.0.

All kinetic measurements were carried out with a Beckman DK1 spectrophotometer and thermostatted 10 cm. optical cells. Solutions were degassed with nitrogen for 10 min. to ensure that all oxygen had been removed, and that the cell contents were at the temperature of the water-bath. An amount of chromium(II) equivalent to the complex was injected from a syringe into the cell through a rubber serum cap; mixing was complete in less than 4 sec. The progress of the reaction was followed at the wavelength of maximum absorption of the complex (460—490  $\text{m}\mu$ ). After the optical density had become constant, a second equivalent of chromium(II) was added, and the rate of reaction was followed at 447  $\text{m}\mu$ , corresponding to a maximum in the spectrum of penta-aquonitrosylchromium(II) ion. Where necessary, a third equivalent of chromium(II) was added, and the reaction followed at the same wavelength. All absorption spectra were recorded automatically, and matched optical cells were used. The concentration of cobalt(II) in the reaction solutions was determined by adding excess of hydrochloric acid and comparing the optical density at 700  $\text{m}\mu$  with that of a similar solution prepared with cobalt(II) carbonate in place of the cobalt(III) complex. At this wavelength, the absorption is due to the tetrachlorocobaltate (II) ion.

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