

Redox Catalysed Substitution Reactions of *trans*-Dichlorobis
(ethylenediamine) cobalt (III) Ions in Aqueous Solution.

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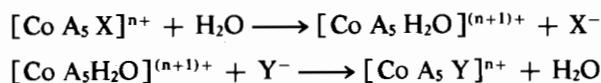
The reaction between pure $\text{trans-[Co en}_2\text{Cl}_2]^+$ and NO_2^- in neutral aqueous solution goes by way of a rate-determining aquation and the final product, $[\text{Co en}_2(\text{NO}_2)_2]^+$, is formed in much the same isomeric ratio as the chloro-aquo complex when formed by direct aquation. In the presence of Co(II) the reaction, after an induction period, is considerably faster and the final product is mainly $\text{trans-[Co en}_2(\text{NO}_2)_2]^+$. In the presence of small amounts of ethylenediamine the induction period vanishes and the reaction is faster still. The kinetic form of this process, when studied under anaerobic conditions, is,

$$-d[\text{Co en}_2\text{Cl}_2^+]/dt = \frac{k[\text{Co en}_2\text{Cl}_2^+][\text{en}][\text{Co(II)}][\text{NO}_2^-]^3}{1 + K[\text{Co(II)}][\text{NO}_2^-]^3}$$

A study of the intermediates and products indicates that the first stage is catalysed and forms $\text{cis-[Co en}_2\text{NO}_2\text{Cl}]^+$ which is converted to $\text{cis-[Co en}_2(\text{NO}_2)_2]^+$ by an uncatalysed aquation-anation path. This then isomerises to $\text{trans-[Co en}_2(\text{NO}_2)_2]^+$ by another catalysed process. It is suggested that the kinetics can be accounted for in terms of the formation of $[\text{Co en}(\text{NO}_2)_3]^-$ as the active catalyst and the first rate-determining step is the redox transfer of chlorine to this from the $\text{trans-[Co en}_2\text{Cl}_2]^+$ cation.

Introduction

The usual mode of ligand replacement in octahedral cobalt(III) complexes in aqueous solution is a two stage process requiring, first of all, the aquation of the complex which is then followed by the anation of the aquo intermediate, e.g.,



Under preparative conditions, when the concentration of Y is large, the second step is fast and the first stage is rate determining. Although this formulation is generally accepted, few cases have been studied in detail.¹ Many years ago, Werner² observed that an

aqueous solution of $\text{trans-[Co en}_2\text{Cl}_2]\text{Cl}$ reacted rapidly with sodium nitrite, provided the solution was not acid, and he used this reaction as a test for the completeness of the conversion of $\text{trans-[Co en}_2\text{Cl}_2]\text{Cl.HCl.2H}_2\text{O}$ to the anhydrous chloride. The rate of this reaction under preparative conditions appeared to be very much faster than the aquation of the *trans*-dichloro cation indicating that an aquation-anation path could not be operating. In view of the work of Pearson, Schmidtke and Basolo³ on the base catalysed reactions of $\text{trans-[Co en}_2\text{NO}_2\text{Cl}]^+$ with nitrite in dimethylsulfoxide and their interpretation of the results in terms of an $\text{S}_{\text{N}}1\text{cb}$ mechanism, we felt that this reaction deserved a closer study. McReynold and Bailar⁴ reported that racemic $\text{cis-[Co en}_2\text{Cl}_2]^+$ reacted instantly with sodium nitrite in aqueous solution whereas the resolved material reacted only slowly, but they then showed that the unresolved material contained catalytic impurities which were removed in the course of the resolution. Since they were able to isolate the $[\text{Co}(\text{NO}_2)_4]^{2-}$ anion from the reaction mixture they concluded that this was the catalyst. Preliminary studies using purified $\text{trans-[Co en}_2\text{Cl}_2]\text{NO}_3$ in dilute aqueous solution indicated that the reaction was not anomalous and did go by way of a rate determining aquation. The fast reaction was therefore catalytic and this paper reports the nature and the kinetics of the catalysis.

Results

(1) *The Uncatalysed Reaction.* The reaction between purified $\text{trans-[Co en}_2\text{Cl}_2]\text{NO}_3$ and sodium nitrite in aqueous solution at 25.0° (pH 7 - 8 unbuffered) was followed spectrophotometrically at 620 m μ . At this wavelength the only species absorbing light to any extent during the reaction is the green starting material and the rate of decrease of optical density was a direct measure of the rate of disappearance of the *trans*-dichloro complex. The process followed a first-order rate law and the first-order rate constant, determined from the slope of $\log_{10}(D - D_{\infty})$ against time (where D is the optical density at time t and D_{∞} is the small residual optical density at the end of the reaction), was essentially independent of the concentration of sodium nitrite. The average rate constant, $4.1 \times 10^{-5} \text{ sec.}^{-1}$

(3) R. G. Pearson, H. H. Schmidtke and F. Basolo, *J. Amer. Chem. Soc.*, 82, 4434 (1960).

(4) J. P. McReynolds and J. C. Bailar Jr., *J. Amer. Chem. Soc.*, 60, 2817 (1938).

(1) F. Basolo, B. D. Stone, J. G. Bergmann and R. G. Pearson, *J. Amer. Chem. Soc.*, 76, 3079 (1954).

(2) A. Werner, *Berichte*, 34, 1734 (1901).

compares well with the rate constant for the aquation of $\text{trans-}[\text{Co en}_2\text{Cl}_2]^+$ in dilute acid at $25.0^\circ\text{C} = 3.5 \times 10^{-5} \text{ sec.}^{-1}$.⁵ The spectrum of the reaction mixture was measured from time to time and, in the presence of a large excess of NaNO_2 (0.1 to 0.2 M) an isosbestic point was found at $534 \text{ m}\mu$. No attempt was made to carry out a spectrophotometric analysis because of the large number of possible species that might be present but the isosbestic point suggested that most of the subsequent steps were fast compared to the first. The final spectrum corresponded closely to that of a mixture of *cis* and *trans-}[\text{Co en}_2(\text{NO}_2)_2]^+ cations with composition $70 \pm 5\%$ *trans* + $30 \pm 5\%$ *cis*. This is very similar to the composition of the kinetically determined product of the aquation of the *trans*-dichloro complex (35% *cis* and 65% *trans*)⁵ and is therefore further indication that the rate determining step is the aquation of the dichloro complex, since there is ample evidence that all the remaining steps of the process occur with complete retention of configuration. For example, the aquation of the *cis* and *trans-}[\text{Co en}_2\text{NO}_2\text{Cl}]^+ isomers takes place without steric change⁶ and there is good reason to believe that the replacement of coordinated water by NO_2^- takes place without fission of the $\text{Co}-\text{O}$ bond (the nitrito intermediate isomerising rapidly to the nitro product).⁷ This too would result in retention of configuration.**

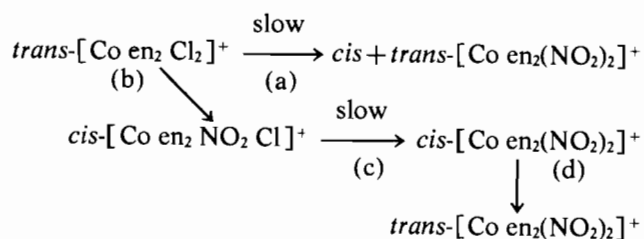
(II) *The Catalysed Reaction.* (IIa) *Intermediates and Products.* Under all conditions of catalysis the reaction took place visibly in two stages. In the first, the green *trans*-dichloro complex changed fairly rapidly into an orange-red intermediate which then, more slowly, was converted to a yellow material. This final product, which could be isolated in good yield as a crystalline perchlorate, as shown, by analysis, to contain the $[\text{Co en}_2(\text{NO}_2)_2]^+$ cation, and examination of the U.V., visible and I.R. spectra indicated that this was often, but not always, the pure *trans* isomer. Occasionally, the product contained up to 10% of the *cis* isomer and, when a significant part of the reaction went by way of the uncatalysed path, the *cis* content of the product was even higher.

The nature of the orange-red intermediate was investigated in a number of ways. (i) Titration of the ionic chloride in the reaction mixture at the end of the first stage indicated that one chloride was liberated for each *trans*-dichloro cation consumed. The second chloride was released in the subsequent slow reaction. (ii) The reaction was stopped when the solution had developed the deep orange colour and an orange-red crystalline perchlorate as obtained in greater than 50% yield from the material remaining when the solution was freeze-dried. When the reaction was carried out with a sufficiently high concentration of complex an identical material was obtained directly on adding perchloric acid to the cooled reaction mixture. This was shown, by analysis, to be $[\text{Co en}_2\text{NO}_2\text{Cl}]\text{ClO}_4$ and the infra-red spectrum was identical to that of an authentic sample of the *cis* isomer. The absorption

spectrum of an aged (fully aquated) aqueous solution was identical to that of a similarly treated solution of the *cis* isomer. Further confirmation was obtained by measuring the rate of aquation of the complex at 25.0° . The observed first-order rate constant, $= 8.7 \times 10^{-5} \text{ sec.}^{-1}$, is much closer to the value reported for the *cis*-chloronitro complex ($1.1 \times 10^{-4} \text{ sec.}^{-1}$)⁶ than it is to that of the *trans* isomer ($1.1 \times 10^{-3} \text{ sec.}^{-1}$).⁶ (iii) In order to ensure that the isolation procedure did not cause any chemical change, the reaction was stopped when the solution was deep orange-red by adding hydrochloric acid and urea (to remove the nitrous acid) to the cooled solution. After the evolution of nitrogen was complete, the mixture was allowed to stand at room temperature until there was no further change of spectrum. Comparison of the final spectrum with those of solutions of the *cis* and *trans-}[\text{Co en}_2\text{NO}_2\text{Cl}]^+ isomers that had been subjected to the same treatment showed that there was close correspondence between the spectra of the materials derived from the reaction product and the *cis*-chloronitro complex. (iv) The spectrum of the reaction mixture was scanned from time to time over the range $400\text{-}600 \text{ m}\mu$ during the first half of the first stage of the reaction. An isosbestic point at $573 \text{ m}\mu$ indicated that no coloured intermediate, other than the *cis*-chloronitro complex was formed in any significant quantity during this part of the reaction.*

The second stage of the reaction is not sensitive to catalysis and appears to go at a rate comparable to that of the aquation of the *cis*-chloronitro complex. Preliminary experiments have shown quite clearly that, under the conditions used in these substitution experiments, the *cis* to *trans* isomerisation of the $[\text{Co en}_2(\text{NO}_2)_2]^+$ cation is catalysed.

One can conclude, therefore, that the following sequence of reactions has been observed.



where reaction (a) is the simple aquation-anation sequence reported above and only observed in the absence of catalyst, (b) is the catalysed reaction whose kinetics are reported below, (c) is a simple aquation-anation process that is unaffected by the catalysts present in the reaction mixture, and, (d) is a catalysed isomerisation which is currently being studied.

This sequence of reactions does not take into account the other reaction intermediates that do not build up in sufficient quantity to be isolated, or even detected spectrophotometrically.

(IIb) *Kinetics of the Catalysed Reaction in the Presence of Oxygen.* In the initial investigation, no attempt was made to exclude oxygen but further work showed that the presence of oxygen had a marked effect upon both the rate and the kinetic form of the reaction. Since we were unable to hold the oxygen content constant, it was not possible to make a detailed in-

(5) M. E. Baldwin, S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 4637 (1961).

(6) S. Ašperger and C. K. Ingold, *J. Chem. Soc.*, 2862 (1956).

(7) R. G. Pearson, P. M. Henry, J. G. Bergmann and F. Basolo, *J. Amer. Chem. Soc.*, 76, 5920 (1954); R. K. Murmann, *ibid.*, 77, 5190 (1955).

vestigation of the reaction under aerobic conditions.

The first set of experiments examining the effect of adding cobaltous chloride to solutions containing the complex and excess NaNO_2 showed that, at the beginning of the reaction, the rate of change of optical density was very small and comparable with that observed in the absence of Co(II) . However, after an induction period, varying between 2 and 40 minutes, the reaction became quite fast. The induction period was not reproducible but there was a general tendency for it to decrease as the concentration of Co(II) increased and also a marked dependence on the amount of dissolved oxygen. Once the fast reaction had started the rate of reaction followed an approximate first-order dependence on the concentration of the *trans*-dichloro substrate and it was possible to obtain a semiquantitative assessment of the rate from the spectrophotometrically determined ($620 \text{ m}\mu$) «first-order» rate constant. By varying each of the components independently it was possible to indicate a rate-law of the form,

— $d[\text{complex}]/dt = k'[\text{complex}]_0[\text{NO}_2^-]^2$, where $[\text{complex}]_0$ is the initial concentration of *trans*- $[\text{Co en}_2 \text{Cl}_2]^+$. Thus, although, in any run the rate law was first-order with respect to complex, the actual rate constant was linearly proportional to the initial concentration of complex. Although the catalysed reaction requires the presence of Co(II) , the rate is independent of $[\text{Co(II)}]$ within the range, $7.6 \times 10^{-3} < [\text{Co(II)}] < 106 \times 10^{-3} \text{ M}$. It was not possible to study the reaction at lower Co(II) concentrations because, under these conditions, the induction period was so long that the major part of the reaction went by way of the uncatalysed process.

A second set of experiments examined the effect of adding small amounts of ethylenediamine to the reaction mixture. This led to a much faster reaction which could be studied at much lower Co(II) concentrations. The most significant observation was that there was no longer an induction period. Under these conditions, when all other concentrations were held constant, the rate of disappearance of the *trans*-dichloro substrate followed a second-order rate law and independent variation of the concentrations of the other reagents indicated a rate law of the form,

$$-d[\text{complex}]/dt = k''[\text{complex}]^2[\text{NO}_2^-]^2[\text{en}][\text{Co(II)}]$$

over the concentration ranges, $[\text{complex}] < 7 \times 10^{-3} \text{ M}$, $[\text{Co(II)}] < 1.27 \times 10^{-3} \text{ M}$, $[\text{en}] < 8.6 \times 10^{-4} \text{ M}$ and $0.133 < [\text{NO}_2^-] < 0.333 \text{ M}$.

The effect of small traces of oxygen upon the catalysed reaction in the absence of ethylenediamine can be seen in Table I.

Oxygen, therefore, slows down the rate of reaction and lengthens the induction period. It is probably responsible for much of the lack of reproducibility.

(IIc) *Kinetics of the catalysed reaction in the absence of oxygen.* The reaction solutions were thoroughly flushed with oxygen-free nitrogen prior to mixing and oxygen was subsequently excluded from the reaction mixture as thoroughly as possible. The reactions fall into three classes, (i), where the solution of the amine and the cobaltous salt was added to the solution of the complex and the nitrite, (ii) where no amine was used, and (iii), where no amine was used and the sodium nitrite was added to the cobaltous solution some 24 hours prior to mixing with the complex. Reactions of type (i) present the clearest picture and will be discussed in detail first. Reactions were carried out in the presence of ammonium acetate, which acted as a buffer and, apart from those reactions where the concentration of nitrite was varied, the ionic strength was held constant.

The progress of the reaction was followed spectrophotometrically at $620 \text{ m}\mu$ where the decrease of optical density corresponds directly to the decrease in the concentration of the *trans*- $[\text{Co en}_2 \text{Cl}_2]^+$ cation. When the reaction was carried out under the conditions described in (i) above, the optical density change followed a first-order rate law. The general kinetic form was obtained by holding all but one of the concentration variables constant and determining the effect on k_{obs} of varying the other.

The dependence of k_{obs} on $[\text{NO}_2^-]$ is shown in Fig. 1 where $\log_{10} k_{\text{obs}}$ is plotted against $\log_{10} [\text{NO}_2^-]$. These points are shown in relation to a line of slope equal to 3.

The dependence of rate upon the concentration of Co(II) is shown in Fig. 2 where k_{obs} is plotted against $[\text{Co(II)}]$ for a series of different ethylenediamine concentrations. The dependence changes from a first-order dependence at the lowest concentrations towards a zero-order dependence at high concentrations. It was shown that this dependence is of the form,

$$k_{\text{obs}} = \frac{A[\text{Co(II)}]}{1 + B[\text{Co(II)}]}$$

and by plotting $1/k_{\text{obs}}$ against $1/[\text{Co(II)}]$ straight lines were obtained of slope $1/A$ and intercept B/A . The

Table I. The effect of dissolved oxygen upon the Co(II) catalysed reaction between *trans*- $[\text{Co en}_2 \text{Cl}_2]^+$ and NO_2^- in aqueous solution at 25.0°

[complex] m. moles/litre	$[\text{NaNO}_2]$ m. moles/litre	$[\text{Co(II)}]$ m. moles/litre	Reaction conditions	k sec. ⁻¹	Induction period (mins)
9.23	166	9.6	oxygen free	0.0184	13.5
9.30	166	9.6	trace of oxygen	0.0115	18.0
9.35	166	9.6	air bubbled through the solution for five minutes before mixing	0.00317	35.0

values of A and B are collected in Table 2 where it will be seen that B is essentially independent of the concentration of ethylenediamine used.

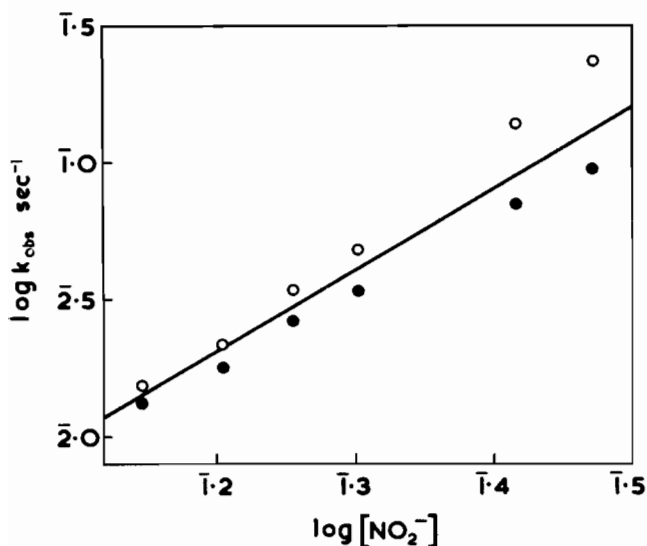


Figure 1. The dependence of k_{obs} on $[NO_2^-]$. ● $\log_{10} k_{obs}$ and ○ $\log_{10}(k_{obs}[1+8 \times 10^4 [Co(II)][NO_2^-]^3])$, all plotted against $\log_{10} [NO_2^-]$. The line drawn has a slope of 3. $[complex] = 7.6 \times 10^{-3} M$, $[en]_{total} = 3.16 \times 10^{-4} M$, $[Co(II)] = 6.73 \times 10^{-5} M$, $[NH_4CH_3CO_2] = 0.133 M$ at 25.0° .

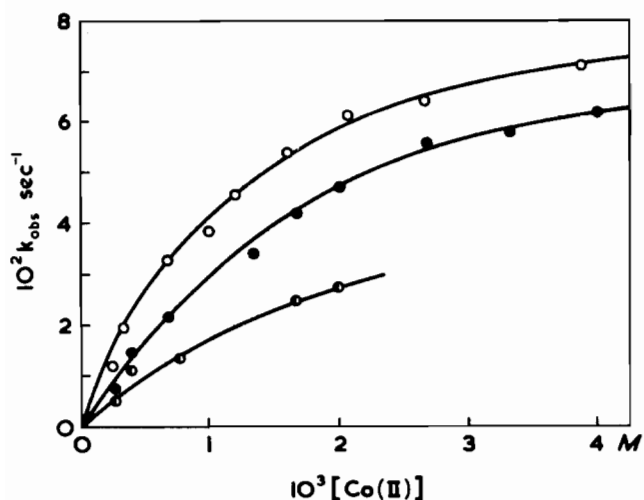


Figure 2. k_{obs} as a function of $[Co(II)]$ in the presence of varying amounts of ethylenediamine. $[en]_{total} = \bullet, 1.45 \times 10^{-4} M$; $\bullet, 2.42 \times 10^{-4} M$; $\circ, 3.36 \times 10^{-4} M$. $[complex] = 7.5 \times 10^{-3} M$, $[NO_2^-] = 0.200 M$ at 25.0°

In deriving a mechanism consistent with the kinetic observations we have produced an expression (*vide infra*) which suggests that B is dependent upon the concentration of nitrite such that $B = K[NO_2^-]^3$. Using the data in Table II we can calculate that $K = 8 \times 10^4 M^4$ and correcting the data in Fig. 1 for the nitrite dependence that appears in the denominator, a second set of points, which are shown in relation to a line of slope 3, are obtained. The significant departure at high nitrite ion concentrations can come from any

Table II. Values of the slope (1/A) and intercept (B/A) of the plots of $1/k_{obs}$ against $1/[Co(II)]$ as a function of the total ethylenediamine added and derived values of A and B, in oxygen-free aqueous solution at 25.0° . $[NaNO_2] = 0.200 M$

[ethylenediamine] m. moles/litre	slope sec. moles/litre	intercept secs.	A $M^{-1} \text{sec.}^{-1}$	B M^{-1}
0.145	0.0320	21.0	31	660
0.242	0.0197	11.6	51	590
0.336	0.0145	9.6	69	660

of a variety of causes but the fast rates and our inability to hold the pH truly constant in this region has prevented us from examining this dependence upon $[NO_2^-]$ in more detail over a wider concentration range.*

The dependence of the rate upon the concentration of ethylenediamine was studied in the presence of $0.133 M$ ammonium acetate. The pH of the reaction mixture was measured while the reaction was in progress and the concentration of free ethylenediamine calculated using the appropriate hydrolysis constant. The relevant data for a series of experiments in which the initial concentrations of all the reagents, except ethylenediamine, were held constant are reported in Table III.

Table III. Pseudo first-order rate constants for the Co(II) and ethylenediamine catalysed reaction between *trans*- $[Co(en)_2Cl_2]^+$ and NO_2^- in aqueous solution at 25.0° in the absence of oxygen. $[NaNO_2] = 0.200 M$, $[Co(II)] = 6.73 \times 10^{-5}$, $[NH_4C_2H_5O_2] = 0.133 M$

[complex] m. moles/litre	pH ^a	total [ethylenediamine] m. moles/litre	free $[en]^b$ ($\times 10^7$) M	$10^3 k_{obs}$ sec. ⁻¹
7.65	7.12	0.316	4.9	8.2
7.72	7.19	0.633	11.5	20.3
8.42	7.18	0.950	17.0	37
8.30	7.24	1.27	26	60
7.71	7.29	1.58	37	93

^a The pH of the solution was measured while the reaction was in progress. It remained constant, or varied only slightly during the first 60-70% of the first stage. ^b The concentration of free (unprotonated) ethylenediamine was calculated using the expression $\log_{10} [en] = \log_{10} [enH^+] - 9.93 + pH$, where 9.93 is the pK_a of ethylenediamine under these conditions. It can also be assumed that $[enH^+] = total [en]$.

The reproducibility of these data is poor, small differences in the measured pH leading to large differences in free $[en]$. In Fig. 3 the variation of k_{obs} with total $[en]$ and also with free $[en]$ is shown and there appears to be a linear dependence upon free $[en]$.

When the ethylenediamine was omitted from the reaction mixture and freshly prepared solutions of the reagents were used for each experiment, much the same behaviour was observed as in the reactions carried out under aerobic conditions. After the induction period the reaction approached a first-order kinetic form and the pseudo first-order rate constants for the disappearance of the *trans*-dichloro complex are given

(* We are indebted to a referee for suggesting this treatment.

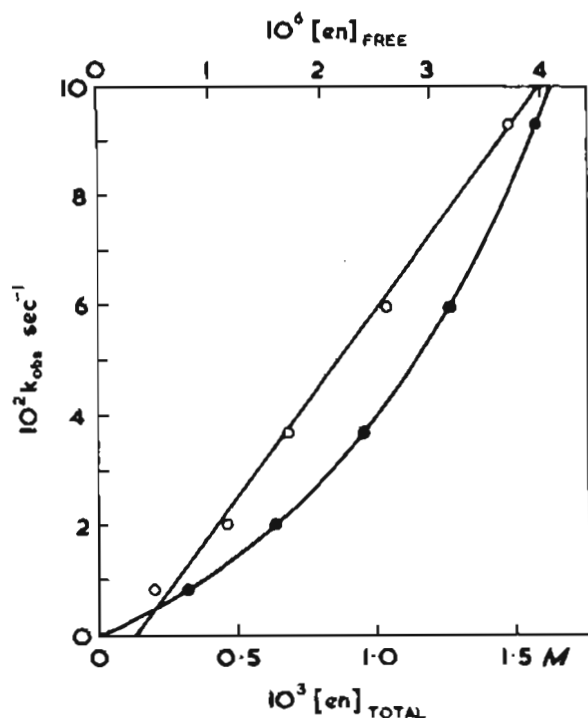


Figure 3. k_{obs} as a function of ethylenediamine concentration. ● and lower scale = $[en]_{total}$; ○ and upper scale = $[en]_{free}$. Data from Table III.

in Table IV as a function of independent variation of $[NO_2^-]$, $[Co(II)]$ and initial concentration of complex. The general rate law for this part of the reaction appears to be,

— $d[\text{complex}]/dt = k_0[\text{complex}][\text{complex}]_0^{1/2}[NO_2^-]^3$, as indicated by the constancy of the term $k_{obs}/[\text{complex}]_0^{1/2}[NO_2^-]^3$ which is listed in the final column of the table. The dependence of rate upon the concentration of $Co(II)$ appears to be negligible,

Table IV. Pseudo first-order rate constants and derived kinetic expression for the $Co(II)$ catalysed reaction between *trans*- $[Co en_2 Cl_2]^+$ and NO_2^- in the absence of ethylenediamine and oxygen, using freshly prepared solutions. (25.0°)

$[complex]_0$ m.moles/ litre	$[Co(II)]$ m.moles/ litre	$[NaNO_2]$ moles/ litre	k_{obs} sec. ⁻¹	k_{obs} [$complex$] ₀ ^{1/2} [NO_2^-] ³
7.36	10.0	0.135	0.0158	78
7.45	10.0	0.166	0.0308	78
7.30	10.0	0.200	0.0545	80
7.81	10.0	0.250	0.102	74
7.48	10.0	0.333	0.222	70
7.82	6.6	0.200	0.0522	74
7.82	10.0	0.200	0.0542	77
7.48	13.3	0.200	0.0550	80
7.60	16.0	0.200	0.0583	84
7.36	20.2	0.200	0.0572	83
5.56	10.0	0.200	0.0533	89
7.60	10.0	0.200	0.0575	82
10.4	10.0	0.200	0.062	76
13.8	10.0	0.200	0.085	90
14.7	10.0	0.200	0.077	79
30.2	10.0	0.200	0.115	83

although there might be a slight increase with increasing concentration. It was not possible to extend the studies to lower concentrations, where some dependence might be expected, because the induction period, which depend upon the amount of $Co(II)$ present, was long enough for most of the reaction to have taken place by way of the uncatalysed path.

A final series of experiments was carried out in much the same way as those described above except that the solutions containing the cobaltous salt and sodium nitrite were mixed some 24 hours before being added to the freshly prepared solution of the complex. Under these conditions reaction commences immediately and the optical density change at 620 $m\mu$ followed a first-order rate law from the beginning. It appears from the rate constants that, although the induction period is no longer observed, the rate of the «first-order» part of the reaction is unaffected by this treatment. In Fig. 4, k_{obs} is plotted against $[Co(II)]$ for the two series of experiments. It will be seen that both sets of data lie on the same curve.

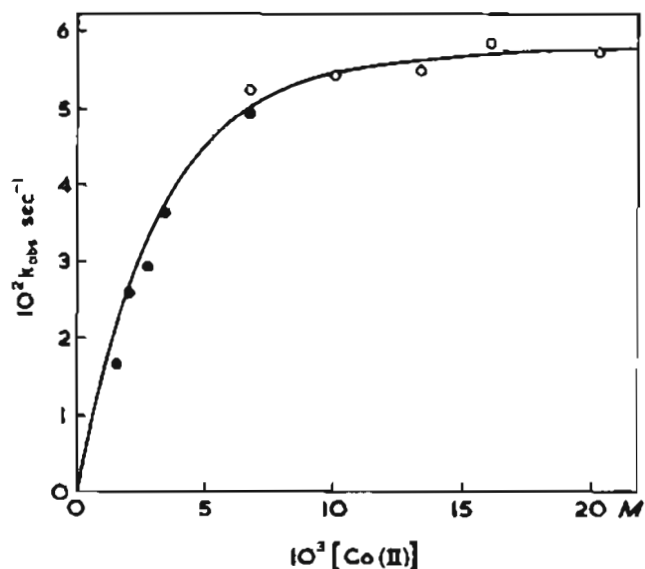


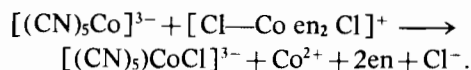
Figure 4. k_{obs} as a function of $[Co(II)]$ for the reaction in the absence of added ethylenediamine. ●, with freshly prepared catalyst solutions, ○, with aged catalyst solutions. $[complex] = 7.5 \times 10^{-3}M$, $[NO_2^-] = 0.200M$ at 25.0°.

Discussion

The overall reaction between *trans*- $[Co en_2 Cl_2]^+$ and NO_2^- is, when catalysed by $Co(II)$ and ethylenediamine, a complicated multi-stage process. It has been possible to demonstrate a catalysed path that yields *cis*- $[Co en_2 NO_2 Cl]^+$ as the first identifiable species, an uncatalysed aquation-anation conversion of this to *cis*- $[Co en_2(NO_2)_2]^+$ and a catalysed isomerisation to the final product, *trans*- $[Co en_2(NO_2)_2]^+$. By following the optical density changes at 620 $m\mu$, it was possible to measure the rate of disappearance of this species and consequently the kinetics and the mechanistic conclusions in this paper refer only to the first stage of the reaction.

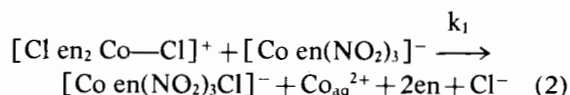
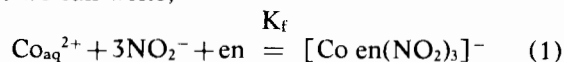
In attempting to understand the mechanism of this reaction we have tried to draw an analogy with the

Co(II) catalysed reaction between *trans*-[Co en₂ Cl₂]⁺ and CN⁻.⁸ In that case a knowledge of the products and of the equilibria in the Co(II) system suggested that the rate determining step was the bridge transfer *redox* process,

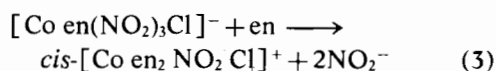


We would therefore like to propose that the first stage of the catalysed nitrite substitution also proceeds by a bridge transfer *redox* process but in this case the reducing agent is [Co en(NO₂)₃]⁻. Whether this is a five-coordinate species or whether H₂O occupies the sixth position is not known.

Thus we can write,



Since we did not observe any significant quantities of any anionic cobalt(III) intermediate, it is suggested that the next stage of the reaction,



is fast. There is no direct evidence to support this assumption but we have previously observed that, when ethylenediamine is added to a cold aqueous solution of Na₃[Co(NO₂)₆] a crystalline material separates after a few minutes. This can be shown to be *trans*-[Co en₂(NO₂)₂][Co(NO₂)₆] and no monoethylenediamine complex anion could be isolated at any stage of the reaction. This would suggest that the rate of entry of the first ethylenediamine is considerably less than that of the second.

Now from equation (1) we can write,

$$[\text{Co en}(\text{NO}_2)_3]^- = K_f [\text{Co}_{\text{aq}}^{2+}] [\text{NO}_2^-]^3 [\text{en}] \quad (4)$$

If the major part of the cobalt(II) is present as the Co_{aq}²⁺ ion then we can ignore the other successive formation equilibria involving Co_{aq}²⁺ and NO₂⁻ and write,

$$[\text{Co}_{\text{aq}}^{2+}] = [\text{Co(II)}]$$

where [Co(II)] represents the total concentration of cobaltous species present in solution and is equal to the amount added at the beginning of the reaction.

Since the ethylenediamine is present in much smaller concentration we cannot make the same assumption and must take into account the various species among which it is distributed. Therefore,

$$[\text{en}]_{\text{total}} = [\text{en}] + [\text{enH}^+] + [\text{Co en}(\text{NO}_2)_3]^- \\ = [\text{en}] + [\text{H}^+][\text{en}]/K_a + K_f[\text{Co(II)}][\text{NO}_2^-]^3[\text{en}] \quad (5)$$

(8) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 966 (1963).

so that,

$$[\text{en}] = \frac{[\text{en}]_{\text{total}}}{1 + [\text{H}^+]/K_a + K_f[\text{Co(II)}][\text{NO}_2^-]^3} \quad (6)$$

in the region of study, [H⁺]/K_a ≫ 1 (approximately = 500) so that (6) simplifies to,

$$[\text{en}] = \frac{[\text{en}]_{\text{total}}}{[\text{H}^+]/K_a + K_f[\text{Co(II)}][\text{NO}_2^-]^3} \quad (7)$$

Now from (2)

$$-d[\text{Co en}_2 \text{Cl}_2^+]/dt = k_1[\text{Co en}_2 \text{Cl}_2^+][\text{Co en}(\text{NO}_2)_3]^- \quad (8)$$

and since, in any one kinetic run [Co en(NO₂)₃]⁻ remains constant,

$$-d[\text{Co en}_2 \text{Cl}_2^+]/dt = k_{\text{obs}}[\text{Co en}_2 \text{Cl}_2^+], \\ \text{where } k_{\text{obs}} = k_1[\text{Co en}(\text{NO}_2)_3]^- \quad (9)$$

Substituting (4) and (7) into (9) and rearranging, we obtain,

$$k_{\text{obs}} = \frac{k_1 K_a K_f}{[\text{H}^+]} \cdot \frac{[\text{Co(II)}][\text{NO}_2^-]^3 [\text{en}]_{\text{total}}}{1 + \frac{K_f K_a}{[\text{H}^+]} [\text{Co(II)}][\text{NO}_2^-]^3}$$

This expression is essentially in accord with the experimentally determined kinetic form bearing in mind that what we have called [en]_{free} in Table III and

$$\text{Fig. 3} = \frac{K_a}{[\text{H}^+]} [\text{en}]_{\text{total}}$$

We have, as yet, been unable to check this hypothesis by a direct and independent examination of the equilibria occurring in aqueous solutions containing Co_{aq}²⁺, NO₂⁻ and ethylenediamine. In fact, the information available in the literature about the solution chemistry of the Co(II)-nitrite system is negligible. No stability constant data are reported and so it is not possible to check the hypothesis that the formation constants are small, however, the lack of any noticeable colour development when sodium nitrite is added to a dilute solution of cobalt(II) chloride (or nitrate) in the complete absence of oxygen, would tend to support this belief. It has been reported⁹ that the species, [Co(NO₂)₅]³⁻, analogous to the corresponding cyanide complex, exists in solution and it is known that salts of the complex anion [Co(NO₂)₆]⁴⁻ are low-spin,¹⁰ but we have been unable to find any direct supporting evidence for the assignment of the formula [Co en(NO₂)₃]⁻

(9) R. J. Gillespie and R. S. Nyholm, *Quart. Revs.*, 11, 377 (1957), quote a private communication from F. Dwyer.

(10) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).

to the active catalyst other than the kinetic observations.

The proposed mechanism would agree with the observation that no evidence could be found for the catalysed conversion of the *cis*-[Co en₂ NO₂ Cl]⁺ cation to the dinitro complex. It has been suggested that the nitro group is a far less efficient bridging group than chloride in the inner sphere redox reactions¹¹ and so the product of the reaction between *cis*-[Co en₂ NO₂ Cl]⁺ and the active catalyst would be precisely the same as that of the reaction with the *trans*-dichloro cation if, in both cases, the chlorine was transferred from the oxidant to the reductant. Such a process, therefore, could not contribute anything to the further progress of the reaction.

When ethylenediamine is initially absent, the reactions between the freshly prepared solutions of the reagents appear to have all the characteristics of an autocatalytic process. If, as seems likely, the nitro and nitrito complexes of cobalt(II) are poor catalysts, either because they are present in small quantity, or else because they are poor reducing agents, we can understand the autocatalysis as arising from the increase in the concentration of ethylenediamine as the cobalt(III) complex is reduced by non-ethylenediamine containing species. We have not examined the kinetics of the process over the whole time scale in sufficient detail to analyse this behaviour adequately and little point is served at this stage by an intensive kinetic study.

The effect of ageing the catalyst mixture upon the kinetics of the reaction is not at all clear. If the ageing allows a more potent catalyst, perhaps a hydrido complex, to form in the Co(II)-NO₂⁻ solution this might explain the absence of an induction period but one would also expect to see the rate of the later stage of the reaction affected. The close agreement between the rate data for the later stages of the reactions using aged and fresh catalysts is surely more significant than mere coincidence.

Experimental Section

Preparations: *cis*-carbonatobis(ethylenediamine)cobalt(III) chloride. Sodium bicarbonate (33.6 g.) and cobalt(II) chloride hexahydrate (23.8 g.) were added, with continuous stirring, to a 10% aqueous solution of ethylenediamine. Hydrogen peroxide (15 ml. of 10% solution) was slowly added and the resultant solution slowly warmed to 80°. After cooling, the solution was filtered and methanol (200 ml.) and acetone (50 ml.) were added to the filtrate which was then cooled further. The deep red precipitate which separated was filtered off, washed thoroughly with methanol and acetone and dried under vacuum over concentrated sulphuric acid.

trans-Dichlorobis(ethylenediamine)cobalt(III) chloride. *cis*-[Co en₂ CO₃]Cl was dissolved in excess concentrated hydrochloric acid and the solution evaporated on a steam bath until a crust of green crystals had formed. On cooling, crystals of the hydrochloride, *trans*-[Co en₂ Cl₂]Cl · HCl · 2H₂O, separated and were

filtered off, washed thoroughly with methanol and acetone, heated to 116° to drive off the hydrogen chloride and recrystallised repeatedly from ethanol-water. The pure material was dried over concentrated sulphuric acid under vacuum.

Found: C, 17.1; H, 6.1; N, 19.9; Co, 20.0; total Cl, 37.2; ionic Cl, 12.4. Co(C₄H₁₆N₄Cl₂)Cl requires, C, 16.8; H, 5.7; N, 19.6; Co, 20.7; total Cl, 37.3; ionic Cl, 12.4%.

A sample of the complex prepared by the longer method of Bailar and Rollinson¹² had, after suitable purification, the same absorption spectrum and showed the same kinetic behaviour.

The presence of Co(II) in this complex was tested for quantitatively by the method of Brown and Steinbach.¹³ A finely ground sample of the complex (0.3 g.) was triturated with concentrated ammonium thiocyanate solution (1 ml.) and the precipitated thiocyanate of the complex filtered off. The filtrate gave no significant test for Co(II). Independent experiments showed that this procedure could give a positive test for 4 × 10⁻⁵ M Co(II), (~ 0.1% of total Co present).

cis-Chloronitrobis(ethylenediamine)cobalt(III) chloride was prepared from *trans*-[Co en₂ Cl₂]Cl by the method of Werner.²

trans-Dinitrobis(ethylenediamine)cobalt(III) nitrate was prepared by the method of Holtzclaw, Sheetz and McCarthy.¹⁴ The perchlorate was obtained by adding solid sodium perchlorate to a saturated aqueous solution of the nitrate.

trans-Chloronitrobis(ethylenediamine)cobalt(III) nitrate was prepared by adding finely powdered *trans*-[Co en₂(NO₂)₂]NO₃ to hot concentrated hydrochloric acid and then warming the resultant paste at 80° until the reaction was complete. The perchlorate was obtained by adding solid sodium perchlorate to a concentrated aqueous solution of the nitrate.

cis-Dinitrobis(ethylenediamine)cobalt(II) nitrate was made by the method of Holtzclaw *et al*¹⁴ and purified by repeated recrystallisation from water.

The *cis*- and *trans*-aquaonitrobis(ethylenediamine)cobalt(III) cations were obtained pure in aqueous solution by allowing the corresponding chloronitro complexes to aquate in neutral aqueous solution at room temperature. The visible and ultraviolet absorption spectra agreed closely with those of Åsperger and Ingold.⁶

Reagents. Reagent grade sodium nitrite was twice recrystallised from a water-methanol-acetone mixture and dried *in vacuo* over concentrated sulphuric acid.

AR grade cobalt nitrate hexahydrate and cobalt chloride hexahydrate were used without further purification.

Ethylenediamine was dried over sodium hydroxide pellets and then distilled from fresh sodium hydroxide, the fraction b.p. 160-161° being collected. Distilled water was saturated with oxygen-free nitrogen and redistilled from alkaline potassium permanganate in an atmosphere of nitrogen. The distillate was also saturated with oxygen-free nitrogen.

(12) I. C. Bailar Jr. and C. L. Rollinson, *Inorg. Synth.*, 2, 222 (1946).

(13) W. B. Brown and J. F. Steinbach, *Anal. Chem.*, 31, 1805 (1959).

(14) H. F. Holtzclaw, D. P. Sheetz and B. D. McCarthy, *Inorg. Synth.*, 4, 176 (1953).

(11) H. R. Ellison, F. Basolo and R. G. Pearson, *J. Amer. Chem. Soc.*, 83, 3943 (1961).

Kinetics. Stock solutions of all reagents, except the *trans*-dichloro complex were made up in advance and stored in volumetric flasks closed with rubber serum caps. Samples were removed as required with a hypodermic syringe. For the slower reactions, the reagent solutions were previously brought to the reaction temperature separately and then added by hypodermic syringe to a capped, black painted volumetric flask that contained a weighed amount of the solid complex. Samples were withdrawn from time to time by means of a hypodermic syringe and run into excess acid in order to quench the reaction. The optical density was then measured at the appropriate wavelength with a Unicam SP 500 quartz spectrophotometer. For the faster reactions, a 2 cm. quartz

spectrophotometer cell was used as the reaction vessel. The solid complex was added and the cell then flushed with nitrogen and sealed with a serum cap. Appropriate amounts of the reagent solutions, previously brought to the reaction temperature were then added and the change in optical density at 620 m μ was recorded as a function of time with a Cary Model 11 recording spectrophotometer.

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