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Mechanism of the Catalytic Reduction of Nitric Oxide with Ammonia by a Solution of Dinitro-(alkyldiamine) Co^{III} Complexes

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It is demonstrated that the reduction of nitric oxide by dinitro-(alkyldiamine) Co^{III} complexes proceeds through the dissociation of the amine group of the alkyldiamine ligand, followed by the formation of mononitrosyl and dinitrosyl intermediate complexes from which N_2 and N_2O are produced, respectively. In aqueous solution, the coordination of NO and NH_3 to the catalytically active intermediate complex is the rate-determining step, which shifts to the reaction of coordinated nitric oxide with ammonia in DMF solution. The stabilities of these intermediate complexes depend on the structure of the alkyldiamine ligands, which cause different selectivities for N_2 and N_2O formation.

Heterogeneous catalytic reduction of nitric oxide by CO, H_2 or NH_3 over various noble metals and metal oxides has been extensively studied and several mechanisms have been proposed.[1,2] Some of these mechanisms involve the dissociation of nitric oxide as an initial step,[3] but in other cases it is considered that surface complexes of nitric oxide and reducing agents are formed.[4] On metal oxides, oxidation of the surface by nitric oxide and its subsequent reduction by reducing agents have been proposed as the catalytic cycle.[5] However, in homogeneous systems this reaction is not well known and only a few systems for the NO–CO reaction have been reported, these including the Rh^{I}–Rh^{III} [6] and Pd^{II}–Cu^{I} [7] redox cycles.

Recently, we reported for the first time[8] that $Co^{III}(LL)_{1-2}(NO_2)_2^+$ ions (LL = ethylenediamine, triethylene tetramine, *etc.*) catalyse the reduction of nitric oxide with various amines, including ammonia, to form nitrogen and nitrous oxide in water, DMF, DMSO, *etc.* Although some mechanisms have been proposed for the NO–NH_3 reaction in heterogeneous systems,[9] it has not been investigated in homogeneous systems. We now report the mechanisms of this reaction in aqueous and DMF solutions obtained using electronic spectra and n.m.r. during the reaction and also kinetic effects due to changing the amine ligands and the solvents.

EXPERIMENTAL

REACTION PROCEDURE

0.1-1 mmol of the complex was dissolved in 100-150 cm^3 of freshly distilled H_2O or DMF and poured into the reaction vessel (250 cm^3 round-bottom flask), which was connected to the closed gas circulation system (total volume *ca.* 400 cm^3).

Before the reaction, the complex solution was thoroughly degassed with repeated freezing by liquid nitrogen. After warming to room temperature, the solution was stirred vigorously using a magnetic stirrer and a mixture of NO + NH_3 gases was introduced onto the catalyst solution. In most experiments with aqueous solutions, concentrated aqueous ammonia was used instead of ammonia gas, the aqueous ammonia being introduced into the complex solution using a pipette in a side arm of the reaction vessel whilst purging the whole system with nitrogen gas. Nitric oxide was purified by repeated distillation between a liquid-nitrogen cold trap and an ethanol slush bath. NH_3 was purified by methanol + dry ice and liquid-nitrogen cold traps.

For the kinetic experiments, a freshly prepared catalyst solution was used for each run and the initial rates of N_2 and N_2O formation were measured, due to the deactivation of the complexes at later stages of the reaction. The analysis of the composition in the gas phase was performed by gas chromatography (molecular sieve 13X for N_2 and NO and Chromosorb 103 for N_2O and NH_3). For isotope-labelled experiments, ^{15}NO (nitrogen-15, purity 96%, from Prochem. B.O.C. Limited) was used without further purification. The isotopic distributions of the products N_2 and N_2O were analysed using a quadrupole mass spectrometer (UTI) with an ionization voltage of 70 eV.

ELECTRONIC SPECTRA AND N.M.R. DURING THE REACTION

For the measurements of electronic spectra during the reaction, another small reaction vessel was used, with a side arm connected through a stopcock to a qualtz cell. The reaction was carried out with the same procedure mentioned above and the spectra at each stage were recorded using a Hitachi 340 spectrophotometer after pouring a part of the solution into the quartz cell.

For n.m.r. experiments, another small vessel was used with several side arms connected to n.m.r. tubes. At each step of the reaction some of the catalyst solution was poured into one of the n.m.r. tubes, which was then cut off from the vessel using a gas burner. N.m.r. measurements were carried out using a R-24B Hitachi n.m.r. spectrometer.

PREPARATION OF THE COMPLEXES

The complexes employed in this study were prepared using a method similar to that reported by Holtzclaw *et al.*[10] In most cases, stoichiometric amounts of the amine solution were added dropwise to an aqueous solution of $Na_3Co(NO_2)_6$. After stirring for several hours, the precipitate was filtered, recrystallized from water and checked by infrared and n.m.r. spectroscopy and elemental analyses. Calculated for $Co(en)_2(NO_2)_3$: N, 30.9; H, 5.1; C, 15.2; found: N, 30.7; H, 5.4; C, 14.8. Calculated for $Co(trien)(NO_2)_3$: N, 27.2; H, 5.5; C, 19.9; found: N, 27.2; H, 6.0; C, 19.6.

RESULTS

REACTIONS OF AQUEOUS SOLUTIONS OF THE COMPLEXES WITH VARIOUS AMINE LIGANDS

The NO–NH_3 reaction was investigated in aqueous solutions of $Co^{III}(LL)(NO_2)_2^+$ complexes with different amine ligands (LL). It was recognized that there are two types of reactions with different diamine or tetramine ligands. When such diamine ligands as $H_2NCH_2CH_2NH_2$, $H_2NCH_2CH_2NH(CH_3)$ and $H_2NCH_2CH_2N(CH_3)_2$, which have at least one primary amine group, were employed in the complex, both N_2 and N_2O were formed without appreciable absorption of NO, as shown in fig. 1. However, when such ligands as $(CH_3)HNCH_2CH_2NH(CH_3)$, $(CH_3)_2NCH_2CH_2N(CH_3)_2$ and triethylenetetramine were used, considerable amounts of NO were absorbed into the solution accompanied by the production of N_2O with a very small amount of N_2, as shown in fig. 2. In the case of the triethylenetetramine complex, a dinitrosyl complex was precipitated due to evaporation of the solution during the reaction. The precipitate had infrared bands at 1880 and 1800 cm^{-1}, characteristic of coordinated dinitrosyl species. However, it could not be purified by recrystallization because of its insolubility after precipitation (analysis, found: N, 25.9; H, 4.7; C, 15.6).

As shown in fig. 1, the reaction did not proceed when only NO or NH_3 was present, which suggests that coordinated NO_2 groups or diamine do not react directly with NH_3 or NO to form N_2 or N_2O. However, to initiate the reaction, NH_3 could be

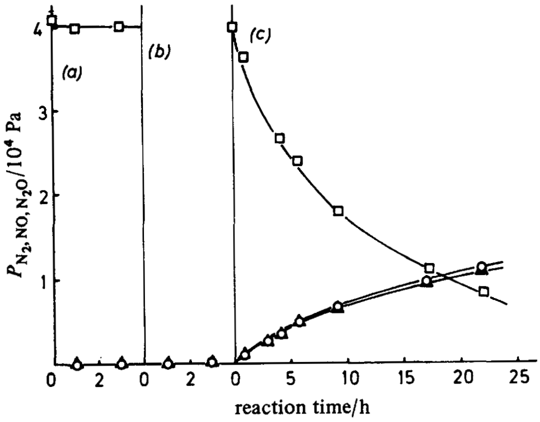

FIG. 1.—NO–NH_3 reaction in aqueous solution of the *cis*-CO(en)$_2$(NO_2)$_3$ complex. $T = 298$ K, 1.6 mmol complex in 100 cm^3 H_2O, $NH_3 = 0.3$ mol. (*a*) Only NO was introduced; (*b*) after the evacuation of NO, NH_3 added to (*a*); (*c*) NO introduced to (*b*). □, NO; ○, N_2; △, N_2O.

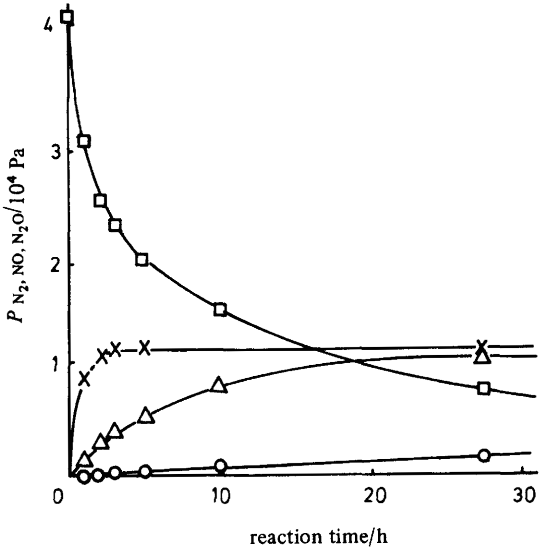

FIG. 2.—NO–NH_3 reaction in aqueous solution of the Co(trien)(NO_2)$_3$ complex. $T = 298$ K, 1.5 mmol complex in 100 cm^3 H_2O, $NH_3 = 0.5$ mol. □, NO; ○, N_2; △, N_2O; ×, total amount of N species fixed in the solution.

substituted for some other amine such as excess ethylenediamine, methylamine, ethylamine, n-butylamine or butylamine. In fig. 3 we see the linear dependence of the initial rates of N_2 and N_2O formation upon the basicity of the amine, which indicates an important role of OH^-. Even NaOH solution could initiate the reaction with nitric oxide to produce N_2 and N_2O but the decomposition of the complex itself caused some unknown black materials to be precipitated in this case.

REACTION KINETICS IN AQUEOUS SOLUTIONS

The initial rates of N_2 and N_2O formation by *cis*-Co(en)$_2$(NO_2)$_3$ complex in aqueous solution depend linearly upon the concentration of the complex and the concentration

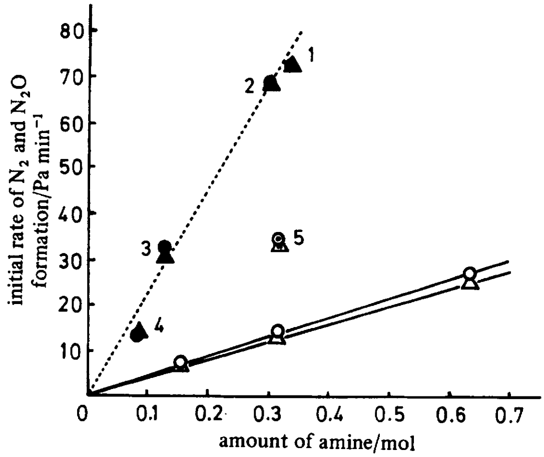

FIG. 3.—Dependences of the initial rates of N_2 and N_2O formation upon the concentration of amines. ○, ⊙, ●, V_{N_2}; △, ◬, ▲, V_{N_2O}. $T = 299$ K, 1.5 mmol $Co(en)_2(NO_2)_3$ in 100 cm^3 H_2O, $P_{NO} = 4 \times 10^4$ Pa. 1, Et_2NH_2 (pK_a = 10.6); 2, $MeNH_2$ (10.7); 3, n-$BuNH_2$ (10.6); 4, Et_3N (10.7); 5, en (9.9); 6, NH_3 (9.3).

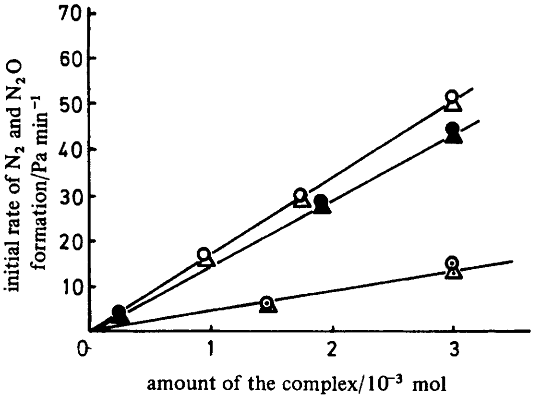

FIG. 4.—Dependences of the inititial rates of N_2 and N_2O formation upon the concentration of *cis*- or *trans*-$Co(en)_2(NO_2)_3$. $T = 299$ K, 100 m^3 H_2O solution, $NH_3 = 0.3$ mol, $P_{NO} = 4 \times 10^4$ Pa. ○, V_{N_2}, and △, V_{N_2O} for [*cis*-$Co(en)_2(NO_2)_2)NO_3$. ●, V_{N_2} and ▲, V_{N_2O} for [*cis*-$Co(en)_2(NO_2)_2]NO_2$. ⊙, V_{N_2} and ◬, V_{N_2O} for [*trans*-$Co(en)_2(NO_2)_2]NO_3$.

of NH_3, as shown in fig. 3 and 4. Fig. 4 also shows that the counter-anions, NO_2^- and NO_3^-, have little effect upon the rate of reaction. On the other hand, fig. 4 shows that there exists a large *trans* effect in this reaction, that is the *cis*-$Co(en)_2(NO_2)_2^+$ complex has a catalytic activity 3-4 times larger than the *trans*-$Co(en)_2(NO_2)_2^+$ complex for the initial rates of N_2 and N_2O formation. This effect may be explained by the electron-withdrawing nature of the nitro group when it is in the *trans* position, which facilitates the nucleophilic attack of OH^- to dissociate the coordinated amine.

Dependence of the reaction rate upon the partial pressure of NO was also examined. As shown in fig. 5, the reaction order was unity with respect to the intial rate of N_2 formation and 1.3-1.5 for N_2O formation. As the reaction proceeded, the complex gradually lost its catalytic activity and over a period of ten catalytic cycles the reaction rate decreased to one-fifth of its initial value. After a long period of reaction, the $Co(en)(NH_3)(H_2O)(NO_2)_3$ complex (analysis, calculated: N, 28.8; H,

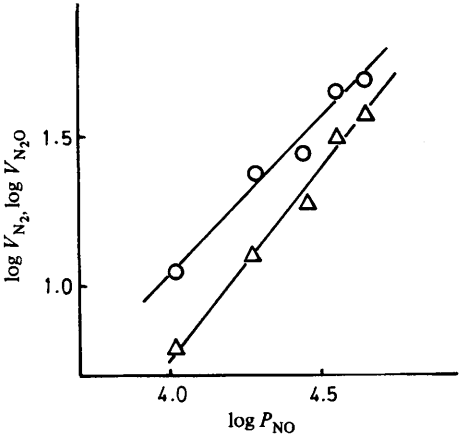

FIG. 5.—Dependences of the initial rates of N_2 and N_2O formation upon the partial pressure of NO. $T = 299$ K, 1.5 mmol *cis*-$Co(en)_2(NO_2)_3$ in 100 cm^3 H_2O, $NH_3 = 0.6$ mol. ○, V_{N_2}; △, V_{N_2O}.

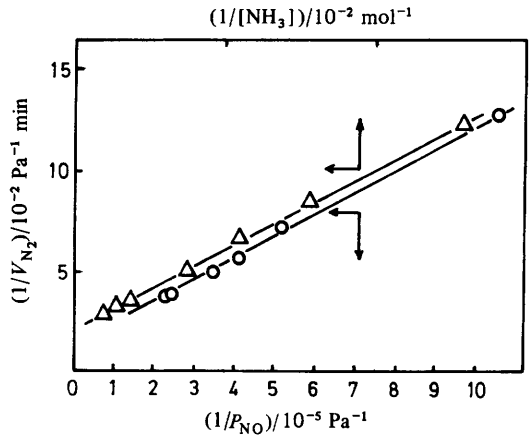

FIG. 6.—Dependences of the initial rates of N_2 and N_2O formation upon the partial pressure of NO and the concentration of NH_3. $T = 298$ K, 0.2 mmol *cis*-$Co(en)_2(NO_2)_3$ in 50 cm^3 DMF, $P_{NO} = 4 \times 10^4$ Pa. ○, V_{N_2}; △, V_{N_2O}.

4.5; C, 8.2; found: N, 29.7; H, 4.8; C, 8.9) was obtained from the catalytic solution, which suggests that the dissociation of ethylenediamine is an important process for this reaction. But the $Co(en)(NO_2)_2^+$ complex itself showed very low catalytic activity.

REACTION IN DMF SOLUTION

When the $Co(en)_2(NO_2)_3$ complex was dissolved in DMF, the catalytic behaviour for the reduction of nitric oxide by ammonia was similar to that in aqueous solution. When only NO or NH_3 was present the reaction did not proceed, but when both of them were introduced into the system, N_2 and N_2O were formed in the manner shown fig. 1. Dependences of the initial rate of N_2 formation upon the concentrations of Co^{3+}, NO and NH_3 were also examined. The rate is proportional to the concentration of the complex and the reciprocal of the rate is inversely proportional to the concentration of NH_3 and to the partial pressure of NO (fig. 6).

The reaction rate in DMF solution is shown much faster than that in aqueous solution when we consider the difference of ammonia concentration in fig. 3 and 6. The effect of added water on the reaction rate in DMF solution was studied and the results are shown in fig. 7. The reciprocal of the rate of N_2 formation is proportional to the amount of H_2O added.

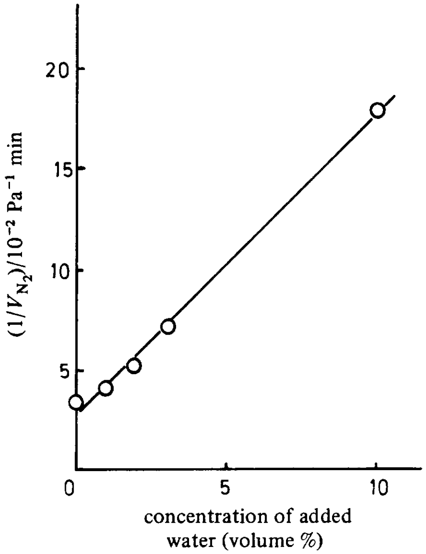

FIG. 7.—Effect of added water on the initial rate of N_2 formation by the *cis*-$Co(en)_2(NO_2)_3$ complex in DMF solution. $T = 299$ K, 0.2 mmol complex in $(50-x)$ cm^3 of DMF and x cm^3 of H_2O, $P_{NO} = 4 \times 10^4$ Pa, $NH_3 = 280$ cm^3.

ELECTRONIC SPECTRA AND N.M.R. DURING THE REACTION

The electronic spectra of the *cis*-$Co(en)_2(NO_2)_3$ complex during the NO–NH_3 reaction in aqueous and DMF solutions were studied. In aqueous solution, the complex has an absorption band around 330 nm, which did not change on addition of NO and NH_3. This is consistent with the kinetic results that the rate-determining step would be the coordination of NO and NH_3 to the original $Co(en)_2(NO_2)_3$ complex. However, in DMF solution the complex possesses an absorption band at 324 nm, as shown in fig. 8. On the addition of only NO or NH_3, this band did not change, but when both NO and NH_3 were added its intensity decreased considerably in 20 min and a new band around 340 nm appeared slowly as the reaction proceeded.

Considering the kinetic results, it is reasonable to suppose that the first decrease in intensity of the band at 324 nm corresponds to the formation of some intermediate complex coordinated with NO and NH_3, while the increase in intensity of the bond at 340 nm corresponds to the deactivation process of the complex, which will be discussed again later. Fig. 8 shows how the spectrum of the *trans*-$Co(en)_2(NO_2)_3$ complex changes; the spectrum initially has an absorption band at 352 nm and undergoes similar changes to those found for the spectrum of the *cis* complex.

Proton n.m.r. spectra of the *trans*-$Co(en)_2(NO_2)_3$ complex in [$^2H_6$]-DMSO solution during the NO–ND_3 reaction are given in fig. 9. The resonance peak at $\delta = 2.4$ can be assigned to a —CH_2— proton of coordinated ethylenediamine and $\delta = 4.7$ to —NH_2. The peak at $\delta = 3.3$ is due to the residual HDO in the solvent. When ND_3

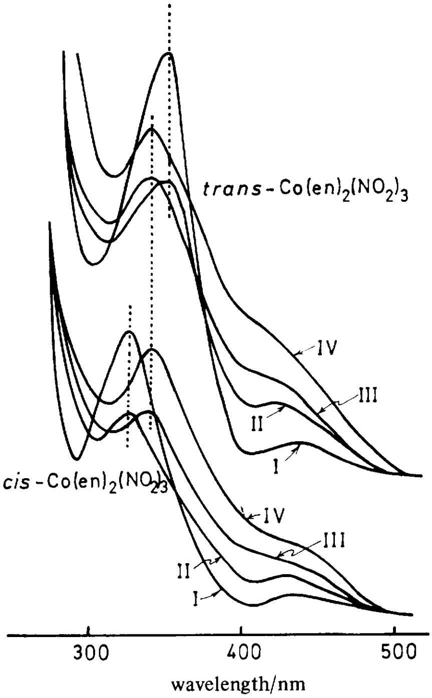

FIG. 8.—Electronic spectra of the *cis*- and *trans*-$Co(en)_2(NO_2)_3$ complex in DMF solution during the NO–NH_3 reaction. $T = 299$ K. I, Spectra of the complexes in DMF solution (no spectrum change was observed when only NO or NH_3 was added); II, $P_{NO} = 4 \times 10^4$ Pa, $NH_3 = 200$ cm^3 added to I, spectrum taken after 10 min; III, after 30 min; IV, after 900 min.

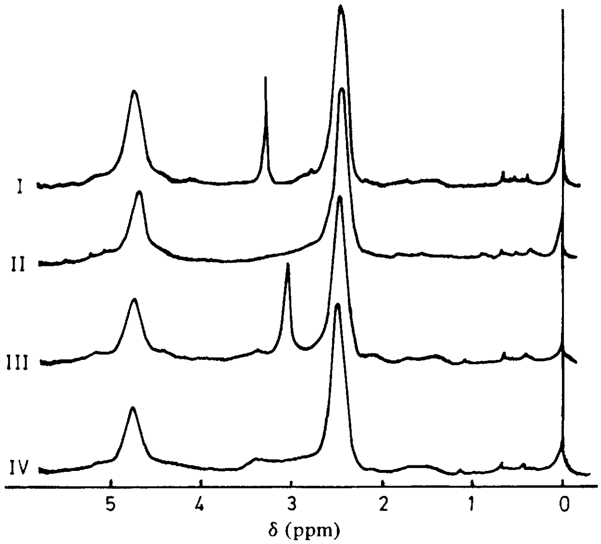

FIG. 9.—N.m.r. spectra (60 MHz) of *trans*-$Co(en)_2(NO_2)_3$ in [$^2H_6$]-DMSO solution during the NO–NH_3 reaction (internal reference: $Me_3SiC_3H_6SO_3Na$). I, Spectra of the complex in [$^2H_6$]-DMSO; II, ND_3 introduced into I; III, NO+ND_3 reaction for 1 h; IV, after exposure to air.

was added to the system, the spectra did not change, except for the disappearance of the peak at $\delta = 3.3$ due to the isotopic dilution of HDO with ND_3. After the addition of NO, a new peak appeared at $\delta = 3.1$, a position intermediate between that for the $-NH_2$ proton of coordinated ethylenediamine ($\delta = 4.7$) and that of free ethylenediamine ($\delta = 1.5$). On exposure of this solution to air, this new peak disappeared completely suggesting that it comes from some intermediate complex formed in the NO–NH_3 reation.

ISOTOPE-LABELLED EXPERIMENTS

To examine the nitrogen sources of the products N_2 and N_2O, the reaction between ^{15}NO and $^{14}NH_3$ was studied in a DMF solution of the $Co(en)_2(NO_2)_3$ complex. As shown in table 1, the N_2 produced was mainly $^{15}N^{14}N$, indicating reaction between ^{15}NO and $^{14}NH_3$ molecules. On the other hand, N_2O was mainly $^{15}N^{15}NO$, indicating reaction between two nitric oxide molecules. These results also suggest that the coordinated nitro group does not participate in the formation of N_2, because the amount of $^{14}N^{14}N$ formed was negligible, considering the purity of ^{15}NO employed (^{15}N, 96%).

TABLE 1.—YIELDS OF ^{15}NO–$^{14}NH_3$ REACTION WHEN CATALYSED BY *cis*-$CO(en)_2(NO_2)_3$ COMPLEX IN DMF SOLUTION

NO conversion	$^{14}N^{14}N$	$^{14}N^{15}N$	$^{15}N^{15}N$	$^{14}N^{14}NO$	$^{14}N^{15}NO$	$^{15}N^{15}NO$
0.18	0.05	0.95	0.00	0.04	0.02	0.94
0.35	0.04	0.96	0.00	0.02	0.02	0.96
0.55	0.03	0.96	0.01	0.01	0.02	0.97
0.73	0.03	0.96	0.01	0.01	0.02	0.97

DISCUSSION

Since the starting $Co(LL)_{1-2}(NO_2)_2^+$ complex is a coordinatively saturated octahedral complex, it is necessary that the dissociaton of some ligand precedes the coordination of NO or NH_3. Because of the necessity of the presence of NH_3 or other bases to initiate the reaction, OH^- seems to play an important role in the dissociation step. The process may be similar to the one postulated in the case of the base hydrolysis of the Co $(en)_2(NO_2)Cl^+$ complex[11,12], cited as a S_N1CB mechanism:

$$Co(en)_2(NO_2)Cl^+ + OH^- \rightleftharpoons Co(en)(en\text{-}H)(NO_2)Cl^+ + H_2O \qquad (1)$$

$$Co(en)(en\text{-}H)(NO_2)Cl^+ \rightleftharpoons Co(en)(en\text{-}H)(NO_2)^+ + Cl^- \qquad (2)$$

$$(en\text{-}H = H_2NCH_2CH_2NH^-).$$

It is reasonable to suppose that step (1) is also present in the case of the $Co(en)_2(NO_2)_2^+$ complex. However, since $Co(en)_2(NO_2)Cl^+$ did not exhibit any catalytic activity for the NO–NH_3 reaction, $Co(en)(en\text{-}H)(NO_2)^+$ cannot be the catalytically active species, which may be formed by the dissociation of one of the NO_2^- groups $Co(en)(en\text{-}H)(NO_2)_2^+$ complex [step (2)]. Consequently, it is necessary to consider some other leaving ligands, which should be one of the coordinated amine groups of ethylenediamine as follows:

$$Co(en)_2(NO_2)_2^+ + OH^- \rightleftharpoons Co(en)(en-H)(NO_2)_2^+ + H_2O \qquad (1')$$

$$Co(en)(en-H)(NO_2)_2^+ + S \rightleftharpoons Co(en)(H_2NC_2H_4\underline{N}H^-)(NO_2)_2(S)^+ \qquad (2')$$

$$Co(en)(H_2NC_2H_4\underline{N}H^-)(NO_2)_2(S)^+ + H_2O \rightleftharpoons Co(en)(H_2NC_2H_4\underline{N}H_2)(NO_2)_2(S)^+ + OH^- \qquad (3)$$

(S = solvent molecule; $\underline{N}$ = dangling amino group).

However, the other amine group of the ethylenediamine should stay on the cobalt cation to maintain the catalytic activity, because $Co(en)(NO_2)_2^+$ showed very low activity for the $NO-NH_3$ reaction.

The proton n.m.r. peak at $\delta = 3.1$, which appeared during the $NO-NH_3$ reaction in DMSO solution, can be assigned to this half-dissociated dangling $—NH_2$ proton, if a rapid exchange motion of coordinated and uncoordinated $—NH_2$ groups is assumed. However, it was impossible to investigate the temperature dependence of the peak due to the DMSO solvent. Another possibility as regards this n.m.r. peak is that hydrogen bonding takes place between the dissociated $-NH_2$ groups and coordinated $—NO_2$, which would reduce the electronic shielding of the $—NH_2$ proton. When only NH_3 was introduced into the catalyst solution, no such peak was observed, which suggests the concentration of this catalytically active $Co(en)(en')(S)^+$ species (en′ = half-dissociated dangling ethylenediamine) is very small under these conditions.

The next step would be the coordination of NO and NH_3 to this half-dissociated ethylenediamine complex, which requires two coordinatively vacant sites. Accordingly it is necessary to suppose the formation of the $Co(en')_2(NO_2)_2(S)_2^+$ complex by the same procedure discussed above:

$$Co(en')_2(NO_2)_2(S)_2^+ + NO + NH_3 \rightarrow Co(en')_2(NO_2)_2(NO)(NH_3)^+. \qquad (4)$$

In aqueous solution, this step seems to be very slow, because the electronic spectra of the complex do not change after the introduction of NO and NH_3. Kinetic data show that the following rate equations are applicable in this case and also support the above consideration:

$$d[N_2]/dt = k[Co^{3+}][NH_3]P_{NO} \qquad (5)$$

$$d[N_2O]/dt = k'[Co^{3+}][NH_3]P_{NO}. \qquad (6)$$

However, in DMF or DMSO solutions, step (4) takes place on the addition of NO and NH_3, as shown by the change in the n.m.r. spectra. The electronic spectra also changed considerably during the $NO-NH_3$ reaction, suggesting the rapid formation of a reaction intermediate. From the results of fig. 6, we propose the following scheme for the reaction in DMF solution (the scheme can also explain the effect of added water):

$$Co(en)_2(NO_2)_2^+ + DMF \overset{K_1}{\rightleftharpoons} Co(en')_2(NO_2)_2(DMF)_2^+$$

$$Co(en)_2(NO_2)_2^+ + H_2O \overset{K_2}{\rightleftharpoons} Co(en')_2(NO_2)_2(H_2O)_2^+$$

$$Co(en')_2(NO_2)_2(DMF)_2^+ + NO + NH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(en')_2(NO_2)_2(NO)(NH_3)^+$$

$$\xrightarrow{k_2} N_2$$

$$V_{N_2} = \frac{k_1 k_2 K_1 [Co^{3+}][NH_3] P_{NO}}{(k_{-1}+k_2)(1+K_1)+K_2(k_{-1}+k_2)[H_2O]+k_1 K_1 [NH_3] P_{NO}} \tag{7}$$

where $[NH_3]$ and $[Co^{3+}]$ represent the concentrations of NH_3 and the complex in the system, P_{NO} is the partial pressure of NO and $[H_2O]$ is the concentration of added water in DMF solution.

From the results of isotope-labelled experiments, it is recognized that N_2 is formed by the reaction between NO and NH_3 and N_2O is formed from the reaction between two NO molecules, suggesting the participation of both mononitrosyl and dinitrosyl intermediate complexes. In the case of the CO (trien)$^{3+}$ complex, some dinitrosyl species could be obtained from the solution during the reaction. But in the case of the CO(en)$_2^{3+}$ complex, only the starting complex and Co(en)$^{3+}$ could be isolated from the solution. When these complexes were impregnated into NaY zeolite, both mononitrosyl and dinitrosyl adsorbed species could be observed by infrared spectroscopy.[13] Consequently, it is reasonable to suppose the existence of these intermediate complexes in the solution.

A plausible reaction mechanism can be proposed as follows:

$$Co(L)_n(NO_2)_2^+ + S \rightleftharpoons Co(L')_n(NO_2)_2(S)_2^+ \tag{8}$$

$$Co(L')_n(NO_2)_2(S)_2^+ + NO + NH_3 \rightleftharpoons Co(L')_n(NO_2)_2(NO)(NH_3)^+ \tag{9}$$

$$Co(L')_n(NO_2)_2(S)_2^+ + 2NO \rightleftharpoons Co(L')_n(NO_2)_2(NO)_2^+ \tag{10}$$

$$Co(L')_n(NO_2)_2(NO)(NH_3)^+ \rightarrow Co(L)_n(NO_2)_2^+ + N_2 + H_2O + (H) \tag{11}$$

$$Co(L')_n(NO_2)_2(NO)_2^+ + 2(H) \rightarrow Co(L)_n(NO_2)_2^+ + N_2O + H_2O \tag{12}$$

where L represents ethylenediamine ($n = 2$) or triethylenetetramine ($n = 1$), S represents an H_2O or DMF molecule and L′ represents the half-dissociated dangling state. From this mechanism, the ratio of N_2 and N_2O formed should be 2 : 1, but experimental results indicate that in the case of the Co(en)$_2^{3+}$ complex this ratio is almost 1 : 1, and that in the case of the Co (trien)$^{3+}$ complex N_2O was the main product and very little N_2 was formed. In order to elucidate these results, it is necessary to introduce another pathway to produce N_2O, which would be the disproportionation of NO to form N_2O and coordinated NO_2:

$$Co(L')_n(NO_2)_2(NO)_2^+ + NO + NH_3 \rightarrow Co(L')_n(NH_3)(NO_2)_3 + N_2O \tag{13}$$

$$Co(L')_n(NH_3)(NO_2)_3 + (H) \rightarrow Co(L)_n(NO_2)_2^+ + N_2 + 2H_2O. \tag{14}$$

Step (13) may be similar to the disproportionation of NO by Co(en)$_2$(NO)Cl$_2$ to form N_2O and coordinated NO_2.[14] Step (14) seems to be very slow and corresponds to the deactivation process of the complexes, giving rise to an absorption peak at 340 nm in fig. 8.

In aqueous solution, step (9) is slow and would be the rate-determining step, consistent with the kinetic data, n.m.r. and electronic spectra. In DMF solution, steps (9) and (10) are now in equilibrium and steps (11) and (12) would be the rate-determining steps at the initial stage of the reaction. The contributions of steps (12) and (13) for the formation of N_2O are comparable in the case of the Co(en)$^{3+}$ complex. However, for the Co(trien)$^{3+}$ complex the Co(trien)(NO$_2$)(NO)$_2^+$ intermediate is stable and step (13) is the main route for the formation of N_2O.

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