Nitrito–Nitro Linkage Isomerisation of the Penta-amminecobalt(III) Complex in Liquid Ammonia

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The nitrito–nitro linkage isomerisation reaction of the penta-amminecobalt(III) complex in liquid ammonia proceeds entirely *via* an intramolecular conjugate-base mechanism. The reaction is fully retentive and the penta-ammine(nitro)cobalt(III) complex is the only species that could be detected by ^1H n.m.r. after the reaction was completed. The advantage of liquid ammonia as solvent is demonstrated by the separate determination of the pre-equilibrium constant $K^{c.b.}$ (ΔH = 27 kJ mol^{-1}; ΔS = −14 J K^{-1} mol^{-1}) and the rate constant of the rate-determining step k_2 ($\Delta H^\ddagger$ = 78 kJ mol^{-1}; $\Delta S^\ddagger$ = 29 J K^{-1} mol^{-1}). Comparison of the activation parameters of the latter rate constant with the activation parameters reported earlier for the ammoniation reactions of a number of cobalt(III) and rhodium(III) amine complexes in liquid ammonia shows the expected deviation from a limiting dissociative activation.

The nitrite ligand shows an *ambident* character:[1] co-ordination to a metal centre can be achieved by either the nitrogen atom or one of the oxygen atoms. In the case of the penta-amminecobalt(III) complex the oxygen-co-ordinated red complex is less stable than the nitrogen-co-ordinated yellow isomer. The kinetics of the spontaneous and the acid-catalyzed isomerisation reaction have been studied extensively, in the solid state,[2,3] as well as in solution.[4-6] Recently, Jackson *et al.*[5] reported that in aqueous solution the isomerisation reaction is subject to base catalysis *via* a conjugate-base (c.b.) mechanism,[7] the actual isomerisation being intramolecular. As liquid ammonia is an excellent solvent to obtain additional information on the mechanism of base-catalyzed solvolysis,[8-12] we have extended the study of this reaction to liquid ammonia as solvent.

Experimental

$[Co(NH_3)_5(ONO)][ClO_4]_2$ was prepared from $[Co(NH_3)_5(H_2O)][ClO_4]_3$ [13] as described in the literature.[14] In order to free the complex from acidic impurities, the perchlorate was dissolved in water (pH 8.5) and filtered into a saturated aqueous solution of sodium perchlorate. Elemental analysis of cobalt and chlorine revealed the purity of the complex to be better than 99%. The complex was stored *in vacuo* over sodium hydroxide and kept at −18 °C in a refrigerator. *trans*-$[Co(NH_3)_4(^{15}NH_3)(ONO)][ClO_4]_2$ was prepared by the action of sodium nitrite on the corresponding *trans*-penta-ammine(aqua)cobalt(III) complex.[15]

Liquid ammonia, potassium perchlorate, and ammonium perchlorate were purified and stored as described previously.[12]

Kinetics.—The isomerisation reaction of $[Co(NH_3)_5(ONO)][ClO_4]_2$ was followed in a closed system under dry nitrogen. The reactions were monitored at 325 and 520 nm on a Beckman UV 5230 spectrophotometer. A detailed description of the apparatus and the data processing procedure has been given elsewhere.[12] All kinetic runs were performed in a constant ionic medium of ClO_4^- (0.20 mol kg^{-1}) by the addition of the calculated amount of potassium perchlorate. The complex concentration was varied from 0.001 to 0.010 mol kg^{-1}. In the runs with added ammonium perchlorate, the acid concentration was varied from 0.001 to 0.010 mol kg^{-1}.

The mean deviation of the fit to a first-order rate law, defined as the mean relative difference between observed and calculated absorbances, was in all cases better than 0.2%. Individual rate constants could be reproduced within 2%. No systematic trends in the residual absorbances were observed for at least five half-lives. The constancy of the temperature was better than 0.1 °C.

Hydrogen-1 *N.M.R.*—The isomerisation reaction of *trans*-$[Co(NH_3)_4(^{15}NH_3)(ONO)][ClO_4]_2$ was monitored on a Bruker WM250 spectrometer, the solvent peak being suppressed by gated decoupling. Solutions were made up in n.m.r. tubes (Wilmad 503-PS) by condensation at −78 °C of *ca.* 0.5 cm^3 NH_3 (enriched with 5% N^2H_3 as internal lock) on the complex. After the tube was sealed off, the spectrum of the starting product was recorded at −50 °C. The reaction mixture was then allowed to reach room temperature, the reaction being completed within one hour. The spectrum of the end product was recorded after cooling to −50 °C again.

Results

The observed rate constants for the nitrito–nitro linkage isomerisation reaction of $[Co(NH_3)_5(ONO)][ClO_4]_2$ in liquid ammonia are plotted as a function of the reciprocal concentration of added ammonium perchlorate in Figure 1. The rate constant follows a linear relation with the reciprocal ammonium concentration. Therefore equation (1) was fitted to the

$$k_{obs.} = k_A + k_B[NH_4ClO_4]^{-1} \qquad (1)$$

observed first-order rate constants. In this equation, k_A denotes the acid-independent and k_B the base-catalyzed contribution to the rate constant. Weighted least-squares fitting revealed k_A to be zero within experimental error. The values obtained for k_B are presented in Table 1. The estimated error for k_B is better than 2%. The results obtained from the kinetic runs without added ammonium perchlorate are given in Figure 2; the observed rate constants are plotted as a function of the reciprocal square root of the total complex concentration ($[complex]_t^{-\frac{1}{2}}$). The concentration dependence of the rate constant is now given by equation (2).

$$k_{obs.} = k_C[complex]_t^{-\frac{1}{2}} \qquad (2)$$

Because of the limited range of complex concentrations that can be used, only a few data are available for each temperature. Therefore we did not fit equation (2) to the observed rate constants, but calculated k_C as the mean value of

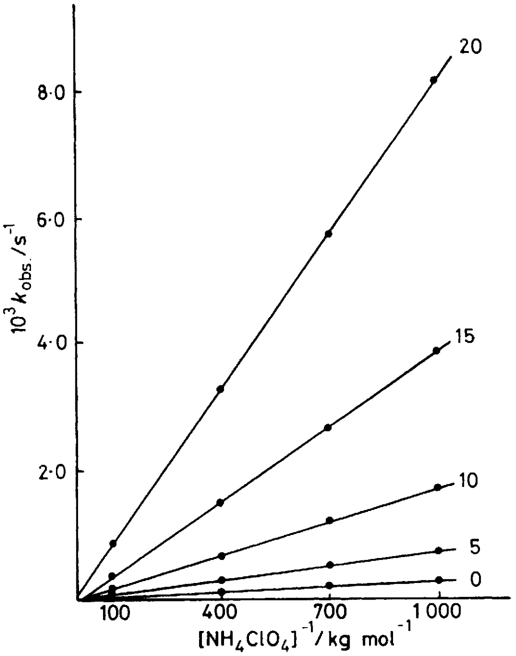


Figure 1. Observed rate constants for the isomerisation *versus* the reciprocal ammonium perchlorate concentration at different temperatures (°C)

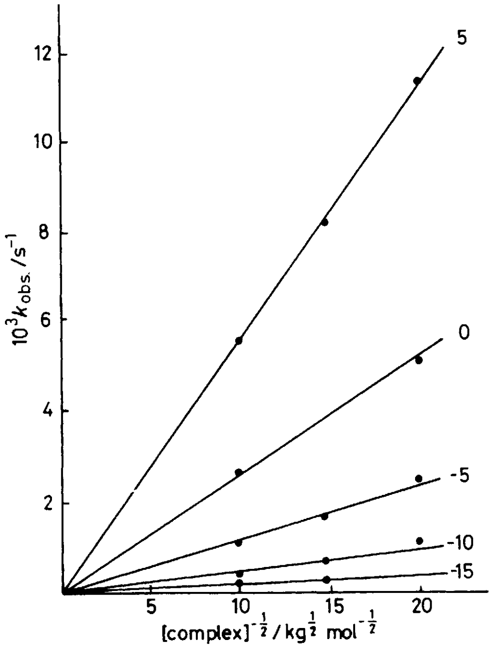


Figure 2. Observed rate constants for the isomerisation *versus* the reciprocal square root of the total complex concentration at different temperatures (°C)

Table 1. Kinetic parameters for the isomerisation in liquid ammonia

Temp. (°C)	10^6k_B/mol kg^{-1} s^{-1} Obs.	10^6k_B/mol kg^{-1} s^{-1} Calc.*	Temp. (°C)	10^4k_C/mol$^{\frac{1}{2}}$ kg$^{-\frac{1}{2}}$ s^{-1} Obs.	10^4k_C/mol$^{\frac{1}{2}}$ kg$^{-\frac{1}{2}}$ s^{-1} Calc.*
20.0	8.11	8.20	5.0	5.62	5.59
15.0	3.85	3.82	0.0	2.65	2.66
10.0	1.76	1.74	−5.0	1.23	1.23
5.0	0.772	0.765	−10.0	0.547	0.554
0.0	0.324	0.328	−15.0	0.244	0.242

* Calculated from the activation parameters of Table 2.

$k_{obs.}[complex]_t^{\frac{1}{2}}$ for each temperature. The values for k_C obtained in this way are presented in Table 1. The mean error in k_C is estimated at 3%.

The results obtained from the kinetic measurements on the isomerisation reaction clearly point in the direction of base catalysis *via* the c.b. mechanism. Realizing that the complex species in liquid ammonia solution are completely associated,[16] the isomerisation is described by reactions (3)—(5); K_1 and

$$[Co(NH_3)_5(ONO)][ClO_4]_2 + NH_3 \xrightleftharpoons{K_1} [Co(NH_3)_4(NH_2)(ONO)]ClO_4 + NH_4ClO_4 \tag{3}$$

$$[Co(NH_3)_4(NH_2)(ONO)]ClO_4 \xrightarrow{k_2} [Co(NH_3)_4(NH_2)(NO_2)]ClO_4 \tag{4}$$

$$[Co(NH_3)_5(NO_2)][ClO_4]_2 + NH_3 \xrightleftharpoons{K_3} [Co(NH_3)_4(NH_2)(NO_2)]ClO_4 + NH_4ClO_4 \tag{5}$$

K_3 refer to rapid acid-base equilibria and k_2 represents the rate-determining step. For the reactions performed without the addition of ammonium perchlorate the first-order rate law is obeyed within 0.2% for at least five half-lives, so that

Table 2. Activation parameters for the isomerisation in liquid ammonia

	$\Delta H^‡$ (ΔH)/ kJ mol^{-1}	$\Delta S^‡$ (ΔS)/ J K^{-1} mol^{-1}
$[K^{c.b.}]^{\frac{1}{2}}k_2$ [a]	91.54 ± 0.5	22.48 ± 1.4
$K^{c.b.}k_2$ [a]	104.84 ± 0.7	15.47 ± 2.1
$K^{c.b.}$ [b]	(27 ± 2)	(−14 ± 4)
k_2 [b]	78 ± 2	29 ± 3

[a] The number of decimals in the activation parameters is determined by the use as regression parameters for the entries in Table 1. The standard deviation given refers as usual to the fit of the experimental data and cannot be given an absolute value without further experiments. [b] Calculated from $[K^{c.b.}]^{\frac{1}{2}}k_2$ and $K^{c.b.}k_2$.

$K_1 = K_3$ within the detection limits, and these constants may be replaced by $K^{c.b.}$, the apparent acid dissociation constant of the substrate.[8] In this case a rate equation of the form (2) is expected with $k_C = [K^{c.b.}]^{\frac{1}{2}}k_2$. For reactions with an excess of added ammonium perchlorate a rate equation of the form (1) is expected,[8] with $k_B = K^{c.b.}k_2$ and $k_A = 0$.

Pseudo-activation parameters for $K^{c.b.}k_2$ and $[K^{b.c.}]^{\frac{1}{2}}k_2$ were calculated by a weighted least-squares method on the basis of the Eyring formula.[17] No significant curvature was found; the results are presented in Table 2, together with the derived activation parameters for k_2 and the thermodynamic parameters for $K^{c.b.}$.

In the ^1H n.m.r. spectrum of *trans*-$[Co(NH_3)_4(^{15}NH_3)(ONO)][ClO_4]_2$ clearly separated signals were observed: a broad singlet at 3.75 p.p.m. (relative to the solvent signal) for the *cis*-$^{14}NH_3$ protons and a sharp doublet at 3.22 p.p.m. [$J(^{15}NH) = 69$ Hz] for the *trans*-$^{15}NH_3$ protons. After the reaction was completed, a singlet for the *cis*-$^{14}NH_3$ protons at 3.49 p.p.m. and a sharp doublet, superposed on the broad singlet, for the *trans*-$^{15}NH_3$ protons at 3.36 p.p.m. [$J(^{15}NH) = 69$ Hz] were observed. A first conclusion that can be drawn

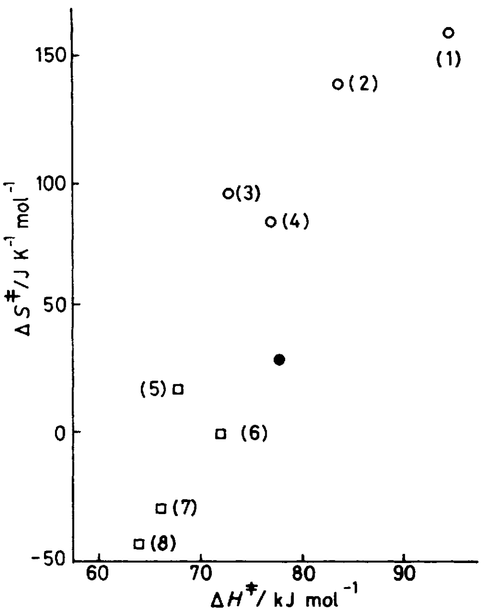


Figure 3. Isokinetic relation for the rate-determining step k_2 in liquid ammonia (data from refs. 8—11): (1) $[Co(NH_3)_5Cl]^{2+}$; (2) $[Co(NH_3)_5(NO_3)]^{2+}$; (3) $[Co(NH_3)_5Br]^{2+}$; (4) *cis*-$[Co(en)_2(NH_3)Cl]^{2+}$ (en = ethylenediamine); (5) $[Rh(NH_3)_5(NO_3)]^{2+}$; (6) *cis*-$[Rh(en)_2Cl_2]^+$; (7) $[Rh(NH_3)_5Br]^{2+}$; (8) *cis*-$[Rh(en)_2(NH_3)Cl]^{2+}$; (●) $[Co(NH_3)_5(ONO)]^{2+}$ (this work)

from these spectra is that the reaction proceeds under complete (>95%) stereochemical retention of configuration, as no *cis*-$^{15}NH_3$ doublet (sharp resonances at 3.35 and 3.63 p.p.m.) was found. Secondly, no hexa-ammine peaks were detected (a second *trans* doublet from $^{15}NH_3$ protons opposite to an ammine group would then be expected), so the reaction product must be the penta-ammine(nitro)cobalt(III) complex.

Discussion

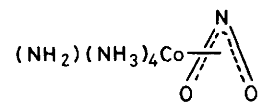
The base-catalyzed nitrito–nitro linkage isomerisation of cobalt(III) amine complexes in aqueous solution proceeds *via* an intramolecular rearrangement of the conjugate base. Extensive evidence for this conclusion has been collected, using various physicochemical measurements.[5,6] The isomerisation reaction in liquid ammonia is expected to proceed *via* the same mechanism. Evidence for this expectation is found in the identification of the end product of the reaction, that was shown to be entirely penta-ammine(nitro)cobalt(III) with the same configuration as the starting material.

Further evidence may be found in the values for the activation parameters of the rate-determining step. The intramolecular retentive mechanism implies that the bond to the NO_2^- ligand is still substantially present in the transition state. This is reflected in the activation entropy found for k_2. If we compare its value (29 J K^{-1} mol^{-1}) with the value found for the ammoniation reaction of, for example,[10] the penta-ammine(nitrato)cobalt(III) complex (139 J K^{-1} mol^{-1}), the absence of the entropy increase due to the liberation of the leaving group [18] in the former reaction is clearly recognized.

In Figure 3 the isokinetic plot is presented of the activation parameters for the rate-determining step [k_2 of reaction (4)] of all base-catalyzed ammoniation reactions of cobalt(III) and rhodium(III) amine complexes in liquid ammonia studied so far. The position of the intramolecular isomerisation reaction of penta-ammine(nitrito)cobalt(III) in this plot displays the similarity in mechanism to the more associatively activated ammoniation reactions of rhodium(III) amines.[10]

The values of the thermodynamic parameters for $K^{c.b.}$ are significantly different from the values determined for other cobalt(III) amines in liquid ammonia. Apparently, the nitro- and nitrito-ligands have similar effects on the acidity of the complex, different from other ligands, including the nitrato-ligand.[10] However, the relatively high values of $K^{c.b.}$ are not reflected in the observed reaction rates, as the value of k_2 is relatively small.

The observations made so far do not bring out major differences between the reactions in water and in liquid ammonia. We therefore assume that in the activated complex the nitrite ligand is π-bonded to the six-co-ordinated metal centre (below), as stated for the aqueous case.[5,6]



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References

1 R. B. Penland, F. J. Lane, and J. V. Quagliano, *J. Am. Chem. Soc.*, 1956, **78**, 887.
2 I. Grenthe and E. Nordin, *Inorg. Chem.*, 1979, **18**, 1109, 1869.
3 A. W. Zanella and A. F. Fucaloro, *Inorg. Nucl. Chem. Lett.*, 1980, **16**, 515.
4 M. Mares, D. A. Palmer, and H. Kelm, *Inorg. Chim. Acta*, 1978, **27**, 153.
5 W. G. Jackson, G. A. Lawrence, P. A. Lay, and A. M. Sargeson, *Inorg. Chem.*, 1980, **19**, 904.
6 W. G. Jackson, G. A. Lawrence, P. A. Lay, and A. M. Sargeson, *J. Chem. Soc., Chem. Commun.*, 1982, 70.
7 F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 177.
8 S. Balt and G. F. Pothoff, *J. Coord. Chem.*, 1975, **4**, 167, 247.
9 S. Balt, J. Breman, and W. de Kieviet, *J. Inorg. Nucl. Chem.*, 1979, **41**, 331.
10 S. Balt and A. Jelsma, *Inorg. Chem.*, 1981, **20**, 733.
11 S. Balt and A. Jelsma, *Transition Met. Chem.*, 1981, **6**, 119.
12 S. Balt, H. J. Gamelkoorn, H. J. A. M. Kuipers, and W. E. Renkema, *Inorg. Chem.*, in the press.
13 E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, 1964, **86**, 1318.
14 M. Linhard, H. Siebert, and M. Weigel, *Z. Anorg. Allg. Chem.*, 1955, **278**, 287.
15 D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, 1967, **89**, 5129.
16 S. Balt and G. F. Pothoff, *J. Solution Chem.*, 1975, **4**, 359.
17 C. F. Detar, 'Computer Programs for Chemistry,' Benjamin, New York, 1969, vol. 3, program ACTENG.
18 S. Balt, *Inorg. Chem.*, 1979, **18**, 333.

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