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A Demonstration of the Absence of Intramolecular Proton Transfer in the Conjugate Bases of *trans*-$[Co(en)_2XY]^{2+/+}$ Complexes

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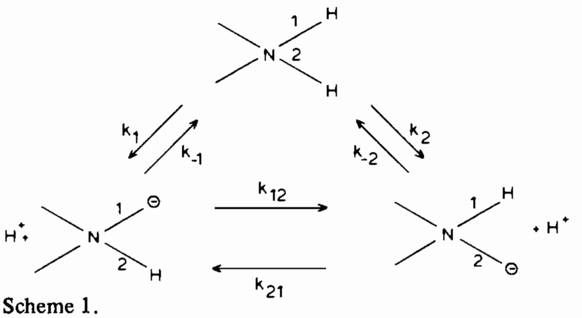
The 'normal' (no rate-limiting deprotonation) conjugate base mechanism [1] for cobalt(III) amine complexes involves a rapid pre-equilibrium, in which the conjugate base is formed by deprotonation, followed by a rate-determining dissociative loss of the leaving ligand. Insight into the intrinsic mechanism, especially the stereochemical aspects, requires knowledge of the fact that deprotonation leads to the reactive conjugate base. The assumption, whether or not the conjugate base, formed in undetectably small quantities, exhibits a rapid intramolecular proton exchange between amine centres, is important when forming conclusions. Since the proposal [2] of intramolecular proton transfer in $[Pt(NH_3)_5NH_2]^{3+}$ was tentatively extended to cobalt(III) amine complexes [3], this matter, especially in relation to the interpretation of experimental exchange results, has been debated [4, 5, 6].

Here we present results showing that no intramolecular proton exchange occurs between the two[*] inequivalent proton sites located on the same nitrogen in the conjugate base of several *trans*-$[Co(en)_2XY]^{2+/+}$ (en = ethylenediamine) complexes (prepared by conventional methods) in liquid ammonia. Liquid ammonia was chosen as solvent because it gives a much better resolution of the $^1H-N<$ (en) chemical shifts and a direct monitoring of the disappearance of the ^1H resonances in N^2H_3 in solution is possible [7].

The reaction for acid dissociation at a coordinated nitrogen centre is given in Scheme 1 (H = ^1H or ^2H).

The principle of microscopic reversibility requires that:

$$\frac{k_1}{k_{-1}}\,\frac{k_{12}}{k_{21}}\,\frac{k_{-2}}{k_2} = 1 \tag{1}$$



Scheme 1.

For simplicity we ignore isotope effects. We define α as the fraction ^1H at site 1 and β likewise for site 2; α and β are averages over a large number of molecules. The complexes are weak acids: $k_{-1}k_{-2} \gg k_1, k_2$. The acid dissociation equilibria are therefore established rapidly compared to the rate of $^1H-^2H$ exchange. Fast proton scrambling in the amido base makes it possible to define one variable, γ, for the average fraction ^1H in the isomeric forms of the base in the above scheme. The rate equation for α is:

$$-\frac{d\alpha}{dt} = k_1\alpha + k_2\alpha - k_2\gamma \tag{2}$$

and similarly for β.

As four concentration variables (including the bulk) are required to describe the proton distribution, the fractions α, β and γ as a function of time will follow relations that are combinations of 3 independent exponentials. A simplification may be introduced by using a steady-state approximation for the two conjugate bases (supposed to be in rapid equilibrium). This gives the relation:

$$k_1\beta - k_1\gamma = -k_2\alpha + k_2\gamma \tag{3}$$

A combination with equation (2) gives:

$$-\frac{d\alpha}{dt} = \left[\frac{k_1^2 + 2k_1k_2}{k_1 + k_2}\right]\alpha - \left[\frac{k_1k_2}{k_1 + k_2}\right]\beta \tag{4}$$

Introduction of the initial conditions $\alpha = \beta = 1$ at t = 0 gives for α (and the symmetrical equation for β):

$$\alpha = \left[\frac{k_1^2 - k_1k_2}{k_1^2 + k_2^2}\right]\exp(-(k_1 + k_2)t) + \left[\frac{k_2^2 + k_1k_2}{k_1^2 + k_2^2}\right]\exp\left(-\frac{2k_1k_2}{k_1 + k_2}t\right) \tag{5}$$

The finding of single-exponential rate laws for $^1H-^2H$ exchange processes at inequivalent sites, occurring at a similar order of magnitude, refutes the assumption of fast intramolecular proton exchange in the conjugate base. Contrary to generally shared assumptions [4, 5], intramolecular proton scrambling does not level out the exchange rates at different sites. Jackson and Begbie came close to this conclusion in a recent publication [6] but these

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[*] The ethylenediamine chelate conformation equilibrium is levelled out on the NMR time-scale. No coalescence is observed, even on heating to room temperature. The amine hydrogens then can be considered as located at 2 groups of 4 equivalent sites, each group situated at one side of the $Co(en)_2$-'plane'.

TABLE I. Exchange Rate Parameters[a] for *trans*-$[Co(en)_2XY]^{2+/+}$ Complexes in N^2H_3.

X; Y	side[b]	$[N^2H_4ClO_4]$[c] (mol kg^{-1})	10^6k^0 (s^{-1})	10^4k^1 (kg mol^{-1} s^{-1})
NH_3[d]; Cl	NH_3	0.005–0.040	1.8 ± 0.2	5.4 ± 0.3
	Cl		0.8 ± 0.1	3.6 ± 0.2
NH_3[d]; N_3	NH_3	0.005–0.040	2.0 ± 0.1	3.2 ± 0.1
	N_3		1.7 ± 0.05	1.03 ± 0.05
$(N_3)_2$		0.001–0.020	1.33 ± 0.02	0.04 ± 0.01
N_3; NCS	N_3	0.002–0.90	4.00 ± 0.05	1.90 ± 0.05
	NCS		1.1 ± 0.1	1.6 ± 0.5

[a] at −60 °C; I(ionic medium; ClO_4^-) = 1.00 mol kg^{-1}; complex concentration 0.10 mol kg^{-1}. [b] Relative to the $Co(en)_2$-plane, indicated by the axial group; assignments are not essential for the present purpose. [c] Acidity range. [d] Coordinated NH_3 exchanges its hydrogens immeasurably fast.

authors apparently did not realize that rapid exchange demands a two-exponential rate law (eqn. (5)). The failure to see this consequence is due to neglect of microscopic reversibility, eqn. (1), that excludes condition (6)*:

$$k_2 \ll k_1 \wedge k_{-1} \simeq k_{-2} \qquad (6)$$

For a number of *trans*-$[Co(en)_2XY]^{2+/+}$ complexes in N^2H_3 we found a strict adherence to a first-order rate law up to 3 half-lives (accuracy of individual resonance integrals 3%, fitting error 5%)†. The first order exchange rate constants showed a linear dependence on the reciprocal acid ($N^2H_4ClO_4$) concentration (eqn. (7); see Fig. 1 for a representative case), expressing general base catalysis, as found before [7, 8].

$$k_{ex} = k^0 + k^1\,[N^2H_4ClO_4]^{-1} \qquad (7)$$

Values for k^0 and k^1 are given in Table I. The generality of first-order behaviour for ^1H–^2H exchange for the present series of *trans*-complexes with a similar order of magnitude of exchange rates at different sites and the strictly individual and linear base dependence, excludes intramolecular proton exchange. As the systems studied offer optimal conditions for the occurrence of exchange, this process seems to be unlikely††.

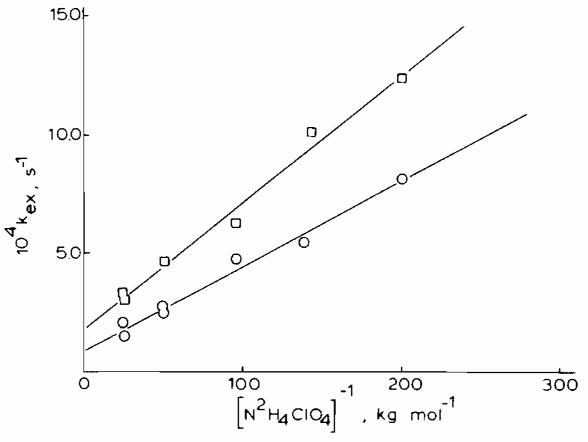

Fig. 1. Variation of the observed ^1H–^2H exchange rate constants with the reciprocal of the ammonium perchlorate concentration for *trans*-$[Co(en)_2(NH_3)Cl](ClO_4)_2$ in liquid N^2H_3. O = Cl^--side; □ = NH_3-side of the $Co(en)_2$-plane (see footnote page L57).

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*The *a priori* possible condition k_2, $k_{-2} \simeq 0$, can also be shown to give a combination of exponentials in the rate law. In the present case it does not lead to exchange at site 2.

†The absence of ammoniation reactions was checked.

††A complete treatment of the more general case of exchange in systems H_aN–NH_b is available on request.