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Activation Volumes for the Two Steps of the Conjugate-Base Mechanism in Liquid Ammonia

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The pressure dependence (10–4000 bar) of the kinetics of the ammoniation of $[Co(NH_3)_5X](ClO_4)_2$ *(*$X = N_3$, *Cl) and the isomerization of* $[Co(NH_3)_5(ONO)](ClO_4)_2$ *in liquid ammonia is reported. The conjugate-base mechanism is operative for these complexes over the entire pressure range used. Activation and thermodynamic parameters were obtained for each of the two steps of the mechanism for* $[Co(NH_3)_5(N_3)](ClO_4)_2$ *at 20 bar. Values for the overall activation volume extrapolated to zero pressure are* $\Delta V^{\ddagger}(0) = -12$ *(11.35 °C, ONO); −20 (24.45 °C,* N_3*) and −30 (0.50 °C, Cl) cm*^{3} *mol*$^{-1}$*. Application of El'yanov and Hamann's empirical relation for the pressure dependence of the ionization of weak acids separates the contributions of the pre-equilibrium (*$\Delta V_{CB}{}^0$*) and the elimination or isomerization reaction (*$\Delta V_2{}^{\ddagger}$*) (at zero pressure). The values obtained for* $[Co(NH_3)_5X](ClO_4)_2$ *are (given as X;* $\Delta V_{CB}{}^0$ *and* $\Delta V_2{}^{\ddagger}$ *in cm*^{3} *mol*$^{-1}$*; T in °C): (ONO; −16 and −1.5; 11.35), (*N_3*; −22 and 1; 24.45), (Cl; −22 and 3; 0.50). These values fit in the accepted picture of volume effects in cobalt(III) ammine kinetics.*

Introduction

The conjugate-base (CB) mechanism is one of the few examples of mechanisms in coordination chemistry for which in-depth understanding has been seriously attempted by a number of groups. A setback to detailed understanding of the intrinsic mechanism is the fact that for the two-step mechanism in aqueous solution no separate determination of activation parameters for the two steps—acid pre-equilibrium and elimination of the leaving group from the conjugate base—can be accomplished.

The higher acidic strength of weak acids and consequently metal amine complexes in liquid ammonia has shown the kinetic and potentiometric evaluation of acid dissociation constants and the ensuing separation of parameters sought [1–3]. This led to the conclusion that, compared to the spontaneous solvolysis, a more favourable $\Delta S^{\ddagger}$ is responsible for the reactivity of the conjugate base [2]. A possibly related, but much more easily visualized activation parameter, is the volume of activation [4] which can be obtained from the pressure dependence of the overall reaction rates:

$$\left(\frac{\delta \ln k}{\delta P}\right)_T = \frac{-\Delta V^{\ddagger}}{RT} \qquad (1)$$

In general $\Delta V^{\ddagger} = \Delta V^{\ddagger}(P)$ will be pressure-dependent. In this paper the pressure dependence (up to 4000 bar) of the ammoniation reactions of $[Co(NH_3)_5X](ClO_4)_2$ ($X = N_3$, Cl) and of the isomerization reaction of $[Co(NH_3)_5(ONO)](ClO_4)_2$ in liquid ammonia is reported. At low pressure ($\leqslant 20$ bar) these reactions proceed via a conjugate-base mechanism. As shown below, this mechanism is also operative at higher pressures for the reactions mentioned.

The conjugate-base mechanism for the complexes studied can be written for $X = Cl^-$ [5] and N_3^- as follows:

$$[Co(NH_3)_5X](ClO_4)_2 + NH_3 \rightleftharpoons [Co(NH_3)_4NH_2X](ClO_4) + NH_4ClO_4 \qquad (2)$$

$K_{CB}, \Delta V_{CB}, \Delta H_{CB}, \Delta S_{CB}$

$$[Co(NH_3)_4NH_2X](ClO_4) \longrightarrow [Co(NH_3)_4NH_2](X)(ClO_4) \qquad (3)$$

$k_2, \Delta V_2{}^{\ddagger}, \Delta H_2{}^{\ddagger}, \Delta S_2{}^{\ddagger}$

In the nitrito–nitro isomerization reaction the rapid pre-equilibrium is followed by an intramolecular rearrangement [6].

The separation of ΔV_{CB} and $\Delta V_2{}^{\ddagger}$ is attempted by using the empirical relation for the pressure-dependence of the dissociation constant of a weak acid, as introduced by El'yanov and Hamann [7]:

$$\ln\left(\frac{K_{CB}{}^P}{K_{CB}{}^0}\right) = -\frac{\Delta V_{CB}{}^0}{RT}\left(\frac{P}{1+bP}\right) = F_1(P) \qquad (4)$$

Here the superscript 0 refers to P = 0; b is an adjustable parameter, for aqueous solution virtually

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independent of the temperature and the nature of the weak acid. Recently, eqn. (4) has been shown to give a better representation of ionization constants in water (up to 8 kbar and 200 °C) than alternative expressions based on the density parameter [8]. As shown below, b is about one order of magnitude larger for liquid ammonia than for water, which makes the application of eqn. (4) at lower pressures possible. If now a quadratic [4] eqn. (5) for the pressure dependence of k_2 is adopted, the overall pressure dependence is given by eqn. (6):

$$\ln\left(\frac{k_2^P}{k_2^0}\right) = -\frac{\Delta V_2^\ddagger}{RT}\cdot P + \frac{\Delta\beta_2^\ddagger}{2RT}\cdot P^2 = F_2(P) \qquad (5)$$

$$\ln\left(\frac{k^P}{k^0}\right) = F_1(P) + F_2(P) \qquad (6)$$

Here the volume of activation, $\Delta V_2^\ddagger$, and the compressibility coefficient of activation, $\Delta\beta_2^\ddagger$, both related to the elimination reaction (3), are defined at zero pressure. It is clear that provided the pressure range studied reaches values of P up to $P = b^{-1}$, the individual parameters ΔV_{CB}^0 and $\Delta V_2^\ddagger$ can be obtained by the application of eqn. (6).

Experimental

The complexes $[Co(NH_3)_5Cl](ClO_4)_2$ [9], $[Co(NH_3)_5(N_3)](ClO_4)_2$ [10] and $[Co(NH_3)_5(ONO)](ClO_4)_2$ [6] were prepared by standard methods and were characterized from their UV/VIS and NMR spectra; elemental analyses revealed the purity of the complexes to be better than 99%. Liquid ammonia, potassium perchlorate and ammonium perchlorate were purified as described earlier [5, 11]. Nitritopentaammineperchlorate was stored in glass ampoules at −70 °C in a refrigerator. All other solids were dried thoroughly before use and stored *in vacuo* over sodium hydroxide.

The ammoniation of $[Co(NH_3)_5(N_3)](ClO_4)_2$ at low pressure (constant at 20 bar) was studied [12] photometrically at 520 nm [6, 11]. In the runs with excess ammonium perchlorate the acid concentration was varied from 0.001 to 0.010 mol kg^{-1} at a constant complex concentration of 5.10^{-3} mol kg^{-1}. In the experiments without added acid the complex concentration was varied between 0.010 and 0.0025 mol kg^{-1} (29 experiments at varying temperature between 0 and 20 °C).

The pressure dependence of the ammoniation of $[Co(NH_3)_5(N_3)](ClO_4)_2$ and $[Co(NH_3)_5Cl](ClO_4)_2$ and the isomerization of $[Co(NH_3)_5(ONO)](ClO_4)_2$ were measured on a Zeiss PMQ II spectrophotometer at 520, 532 and 520 nm. The spectrophotometer was connected with light guides to a high-pressure cell, part of a home-made high-pressure apparatus [13]. The temperature could be kept constant to within 0.05 °C. The reactions were studied as a function of pressure at the following complex and ammonium perchlorate concentrations and temperatures. $[Co(NH_3)_5(ONO)](ClO_4)_2$: 0.010 mol kg^{-1}; 0.01 and 0.005 mol kg^{-1}; 11.35 °C. $[Co(NH_3)_5(N_3)](ClO_4)_2$: 0.005 mol kg^{-1}; 0.00125; 0.002 and 0.005 mol kg^{-1}; 24.45 °C. $[Co(NH_3)_5Cl](ClO_4)_2$: 0.015 mol kg^{-1}; 0.10 and 0.05 mol kg^{-1}; 0.50 °C. Furthermore, the reactions of azidopentaamminecobalt(III) perchlorate and nitritopentaamminecobalt(III) perchlorate were studied as a function of temperature under the conditions: P = 3200 bar and $[NH_4ClO_4]$ = 0.002 mol kg^{-1} (N_3) or 0.01 mol kg^{-1} (ONO).

All kinetic runs were performed at a constant ionic medium [3, 5] of 0.2 mol kg^{-1} by the addition of the calculated amount of potassium perchlorate. In this ionic medium the ammine complexes can be considered as completely ion-paired [14]. 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 0.5%.

Results

The conjugate-base mechanism has been proved to be operative at low pressures (<10 bar) for the ammoniation of $[Co(NH_3)_5Cl]^{2+}$ [5] and the isomerization of $[Co(NH_3)_5(ONO)]^{2+}$ [6]. Under conditions of excess added acid (NH_4ClO_4), the reported reactions follow the rate law deduced on the basis of the CB mechanism:

$$k_{obs} = K_{CB}k_2[NH_4ClO_4]^{-1} \qquad (7)$$

Apparently a similar relation holds for the ammoniation of $[Co(NH_3)_5(N_3)](ClO_4)_2$ at low pressure over a range of temperatures (Fig. 1) and up to high pressures (Fig. 2). Consequently, the CB mechanism is operative over the entire pressure range studied.

Activation parameters were obtained by a least-squares analysis on the basis of eqn. (7) and the Eyring formula. No systematic deviations were found. The resulting values are in Table I.

For the comparative temperature-dependence study of the azido and the nitrito compounds at 3200 P, a single experiment was performed at each temperature for a fixed acid concentration, from which $K_{CB}k_2$ was calculated, using eqn. (7) (Table II); from these values the activation parameters were calculated.

For the ammoniation reactions of the azido complex, performed without the addition of ammonium perchlorate, the fact that a first-order rate law is obeyed means that K_{CB} has the same value for the initial and the final ammine ($[Co(NH_3)_6](ClO_4)_3$)

TABLE I. Thermodynamic and Activation Parameters[a] for the Reactions[b] of $[Co(NH_3)_5X](ClO_4)_2$ at Constant Ionic Medium (0.2 mol kg^{-1}).

X	P bar	$\Delta H(K_{CB}k_2)$	$\Delta S(K_{CB}k_2)$	ΔH_{CB}	ΔS_{CB}	$\Delta H_2^{\ddagger}$	$\Delta S_2^{\ddagger}$	ref.
ONO(Is)	'0'[c]	105	15	27	−14	78	29	6
ONO(Is)	3200	119 ± 3	71 ± 9					d
N_3(A)	20	92 ± 2	−58 ± 4	−4 ± 3	−134 ± 9	96 ± 3	76 ± 9	12
N_3(A)	3200	106 ± 3	−6 ± 9					d
Cl(A)	'0'[c]	87	−13	−8	−172	95	159	5

[a] H in kJ mol^{-1}; S in J K^{-1} mol^{-1}. [b] A = Ammoniation; Is = Isomerization. [c] Ambient pressures (no external pressure). [d] This work.

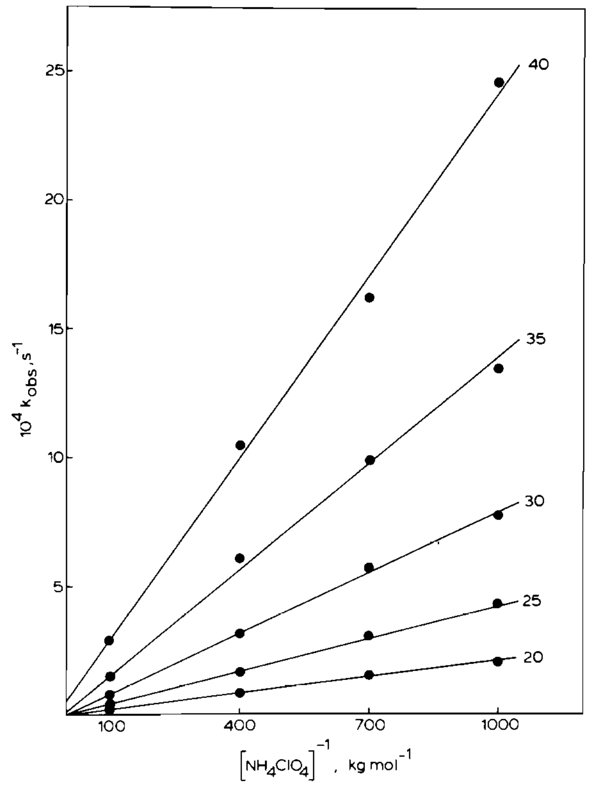

Fig. 1. Variation of the observed rate constant of ammoniation with the reciprocal of the ammonium perchlorate concentration for azidopentaamminecobalt(III) perchlorate, at different temperatures (in °C) and a constant ionic medium of 0.2 mol kg^{-1}.

within experimental error [15]. Then the observed rate constant is given by eqn. (8); in

$$k_{obs} = (K_{CB})^{1/2} k_2 [Co]_t^{-1/2} \qquad (8)$$

this equation $[Co]_t$ indicates the total complex concentration.

Pseudo activation parameters were obtained directly by subjecting $k_{obs} \times [Co]_t^{+1/2}$, *i.e.* $(K_{CB})^{1/2}k_2$,

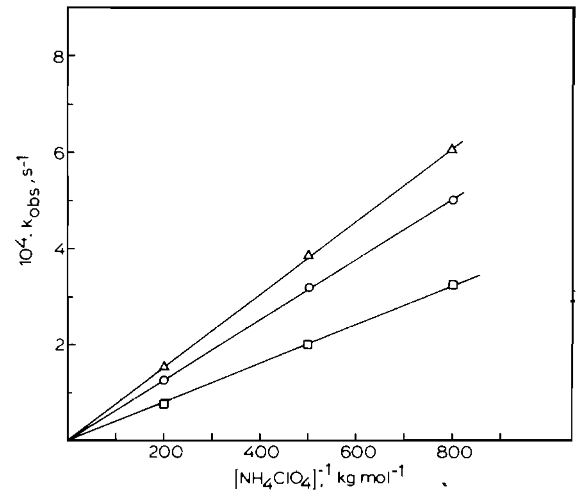

Fig. 2. Variation of the observed rate constant of ammoniation of azidopentaamminecobalt(III) perchlorate *versus* the reciprocal ammonium perchlorate concentration at different pressures (□: 50 bar, ○: 1000 bar, △: 3500 bar). All runs performed at T = 24.45 °C and a constant ionic medium of 0.2 mol kg^{-1}.

TABLE II. Observed Rate Constant (expressed as $K_{CB}k_2$) as a Function of Temperature at Constant Pressure (3200 bar) and Constant Ionic Medium (0.2 mol kg^{-1}).

Compound	T °C	$10^6 K_{CB}k_2$ mol kg^{-1} s^{-1}
$[Co(NH_3)_5N_3](ClO_4)_2$	11.75	0.111
	18.60	0.322
	24.45	0.759
	29.80	1.72
$[Co(NH_3)_5(ONO)](ClO_4)_2$	7.10	2.02
	7.45	2.05
	10.50	3.72
	11.35	4.70
	15.70	9.15
	17.05	11.1
	19.20	17.4
	19.60	18.8

TABLE III. Observed Rate Constant (expressed as $K_{CB}k_2$) as a Function of Pressure at a Constant Ionic Medium (0.2 mol kg^{-1}).

$[Co(NH_3)_5(N_3)](ClO_4)_2$		(24.45 °C)	$[Co(NH_3)_5(ONO)](ClO_4)_2$		(11.35 °C)	$[Co(NH_3)_5Cl](ClO_4)_2$		(0.50 °C)
P bar	$[NH_4ClO_4]^{-1}$ mol^{-1} kg	$10^6 \cdot K_{CB}k_2$ mol kg^{-1} s^{-1}	P bar	$[NH_4ClO_4]^{-1}$ mol^{-1} kg	$10^5 \cdot K_{CB}k_2$ mol kg^{-1} s^{-1}	P bar	$[NH_4ClO_4]^{-1}$ mol^{-1} kg	$10^4 \cdot K_{CB}k_2$ mol kg^{-1} s^{-1}
			60	200	0.24	15	20	0.27^5
115	200	0.47^5	75	100	0.25^5	35	20	0.28^5
165	500	0.45^5	320	200	0.28^5	90	10	0.30
175	800	0.50	325	100	0.28	95	20	0.30^5
300	500	0.51^5	750	100	0.35^5	130	20	0.31^5
525	200	0.58^5	1050	200	0.36^5	210	10	0.32^5
670	200	0.57	1570	200	0.40^5	250	20	0.33
900	500	0.61	1580	100	0.38	320	10	0.34^5
1030	800	0.62	2040	200	0.43^5	325	20	0.32^5
1150	500	0.62^5	2055	100	0.44^5	510	10	0.34
1225	200	0.64	2900	100	0.50	795	20	0.36^5
1450	200	0.71	2950	200	0.45^5	1070	20	0.38
1500	200	0.67^5	3060	100	0.47	1240	10	0.38
1510	500	0.66^5	3135	200	0.44^5	2045	20	0.38
2020	200	0.73	4075	100	0.52	2615	20	0.38
2530	200	0.76	4290	200	0.50	2640	10	0.39
2580	800	0.76^5				3080	10	0.39
						4025	20	0.36

TABLE IV. Parameters[a] Describing the Pressure Dependence of the Reaction[b] Rates for $[Co(NH_3)_5X](ClO_4)_2$ at Constant Ionic Medium (0.2 mol kg^{-1}).

X	T °C	ΔV_{CB}^0	$\Delta V_2^\ddagger$	$\Delta V^\ddagger (P = 0)$[c]	10^3 b bar^{-1}
ONO(Is)	11.35	−16 ± 2	−1.5 ± 0.5	−12 ± 2	1.1
N_3 (A)	24.45	−22 ± 4	1.0 ± 0.5	−20 ± 3	1.0
Cl (A)	0.50	−22 ± 6	3 ± 1	−30 ± 4	1.0

[a] V in cm^3 mol^{-1}. [b] Is = Isomerization; A = Ammoniation. [c] Extrapolated by a polynomial regression method (see Text).

determined at different complex concentrations and different temperatures, to a least-squares activation analysis. The resulting parameter values are presented in Table I.

The variation of the ammoniation and isomerization rates with pressure at conditions of excess acid is presented in Table III as $K_{CB}k_2$ values calculated from eqn. (7). The use of eqn. (7) again is vindicated from the acid independence of values obtained at the same or comparable pressures. To determine the volume of activation at zero pressure, $\Delta V^{\ddagger}(0)$, without using explicit assumptions, each set of ln $(K_{CB}k_2)$ *versus* P data was subjected to a polynomial regression analysis. The expansion of the degree of the polynomial was terminated when the F test on the significance of the added term was below the 99% probability limit: the whole procedure was then repeated, leaving out one or more points at the high-pressure side. After that the procedure was repeated again, leaving out more points until only a few points were left at the low-pressure side of the data, with which the procedure was repeated for the last time. The series of values for the rate constants k^0 (P = 0 bar) and for the activation volumes $\Delta V^{\ddagger}(0)$, calculated in this way, converge. The values for $\Delta V^{\ddagger}(0)$ are given in Table IV.

Secondly, the three sets of ln $(K_{CB}k_2)$ *versus* P data were subjected to a three parameter fit on the basis of eqn. (6), using a Marquardt routine [16] and the k^0 values obtained in the extrapolation procedure described above. The quadratic term gave no significant contribution to the fit (on the basis of a F test significance analysis). The fit had a reasonably small mean error of 8% in the case of the nitrito and the azido complex, but was significantly larger (18%) for the chloro complex. The ensuing parameter values are in Table IV. Figure 3 gives a comparison between experimental and calculated rate constants.

Recent experiments at pressures up to 6000 bar (0.80 °C) [17] again revealed the pronounced maximum in the ln k^P *versus* P plot and a subsequent continuous decrease of k reaching about 15% at 6000 bar. By this the presence of positive values for the activation volume of the elimination reaction, $\Delta V_2^{\ddagger}$, is even more clearly exhibited.

Discussion

The assumption of the identity of the CB mechanism from low to high pressures is borne out by the continuous application of eqn. (7) (Fig. 2) and by the changes observed in the activation parameters for $K_{CB}k_2$ on increasing the pressure. The nitrito and the azido reactions show similar changes in both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, exhibiting a compensatory effect taken as an indication for the identity of the mechanism. Further, the originally empirical relation used for the pressure dependence of K_{CB} (eqn. (4)) can, as worked out by El'yanov and Hamann [7], be derived from a simple electrostatic theory of ion solvation in which the decisive factor is the pressure dependence of the dielectric constant ϵ of the solvent, given by eqn. (9). In this equation the constant b

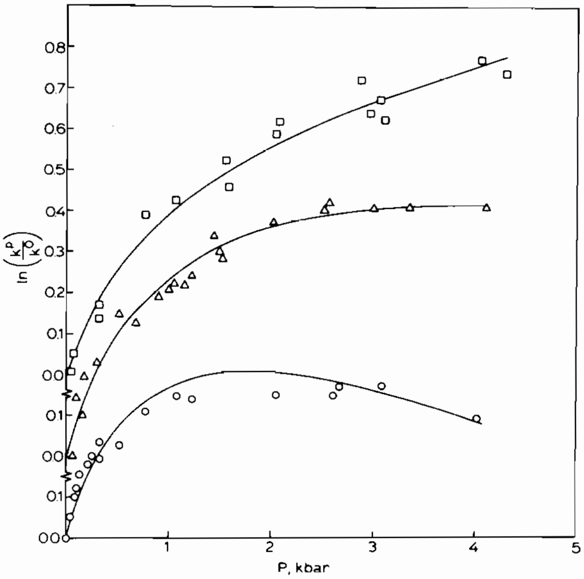

Fig. 3. ln (k^P/k^0) *versus* P for $[Co(NH_3)_5(N_3)](ClO_4)_2$ at 24.45 °C (△); $[Co(NH_3)_5(ONO)](ClO_4)_2$ at 11.35 °C (□) and $[Co(NH_3)_5Cl](ClO_4)_2$ at 0.50 °C (○). Drawn lines represent the least-squares fit according to eqn. (6). Note the shift of the ordinate for the different compounds.

$$(\epsilon^P)^{-1} - (\epsilon^0)^{-1} = -\text{constant}\left[\frac{P}{1 + bP}\right] \qquad (9)$$

is the same as in eqn. (4). This provides a check on the model. El'yanov and Hamann found for aqueous solutions b = 9.4×10^{-5} bar^{-1} from the dielectric constant and b = 9.2×10^{-5} bar^{-1} for a number of weak acids [7].

Using published values [18] we fitted the pressure dependence of the dielectric constant of ammonia to eqn. (9), giving b = $(0.6 \pm 0.1) \times 10^{-3}$ bar^{-1} (25 °C). The agreement with the kinetic result: b = 1×10^{-3} bar^{-1} is not as good as for water, but is still satisfactory. Even more satisfying is the independence of b from the nature of the ammine complex and the temperature. The fact that b is about one order of magnitude larger for ammonia than for water makes an analysis on the basis of eqn. (4) possible at moderate pressures in the former solvent.

If the analysis of the pressure data on the basis of El'yanov and Hamann's formula is accepted, a comparison of the entries in Table I and Table IV makes it clear that for the present set of reactions in liquid ammonia no relation exists between $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ in the line of Twigg [19]. It is especially striking that the extraordinarily large values for $\Delta S^\ddagger$ generally found in our laboratory for ammoniation reactions [2, 3, 5] are not reflected in $\Delta V_2{}^\ddagger$. We do not know what role ion association (being virtually complete in the medium employed [14]) plays in this respect. Remarkably, the magnitude of $\Delta V_2{}^\ddagger$ of ammoniation (1–3 $cm^3\ mol^{-1}$) is comparable to $\Delta V^\ddagger$ for the aquation of *trans*-$CoN_XCl_2{}^+$ complexes of the same charge type [20], that also do not show a relation between $\Delta S^\ddagger$ and $\Delta V^\ddagger$. Moreover, $\Delta V_2{}^\ddagger$ for the nitrito–nitro isomerization (–1.5 $cm^3\ mol^{-1}$) is not far from the values reported for the first isomerization step of the similarly-charged *cis*- and *trans*-$[Co(en)_2(ONO)_2]^+$ ions in aqueous solution (–5.6 and –3.6 $cm^3\ mol^{-1}$ respectively) [21]. This state of affairs may seem contradictory to the more extensive electrostriction expected for liquid ammonia. The reason could be a quenching of these effects due to complete ion-pairing.

Construction of a volume profile is hampered by the fact that no density data on metal complexes or NH_4ClO_4 in liquid ammonia are available. Only a few data on simple salts have been published [22]. For reactions (2) and (3) we have, respectively:

$$\begin{aligned}\Delta V_{CB}{}^0 = {} & \bar{V}([Co(NH_3)_4(NH_2)X]\cdot(ClO_4)) - \\ & - \bar{V}([Co(NH_3)_5X]\cdot(ClO_4)_2) + \\ & + \bar{V}(NH_4ClO_4) - V(NH_3) \qquad (10)\end{aligned}$$

$$\Delta V_2{}^\ddagger = \bar{V}^\ddagger - \bar{V}([Co(NH_3)_4(NH_2)X]\cdot(ClO_4)) \qquad (11)$$

Here $\bar{V}^\ddagger = \bar{V}([Co(NH_3)_4(NH_2)]\cdot(X)(ClO_4))$, assuming that X^- has not left the second coordination sphere on activation [2, 23].

Following the arguments presented originally by Sisley and Swaddle [9], we take the effective molar volume of an ammine ligand coordinated to cobalt(III) to be 18 [24] $cm^3\ mol^{-1}$. Consequently:

$$\bar{V}^\ddagger = \bar{V}([Co(NH_3)_5(NH_2)]\cdot(X)(ClO_4)) - 18 \qquad (12)$$

Further, the nearest model compound for NH_4ClO_4, found in the literature of density data for liquid ammonia, is NH_4I. Extrapolating Gunn and Green's [22] molar volume data to 0.2 mol kg^{-1}, using the semiempirical relation given by the authors, gives $\bar{V}(NH_4I) = 23$ $cm^3\ mol^{-1}$ (0.2 mol kg^{-1}, 0 °C). Putting the data for X = Cl at 0 °C ($\Delta V_{CB}{}^0 = -22$; $\Delta V_2{}^\ddagger = 3$; and $V(NH_3) = 27$ $cm^3\ mol^{-1}$) into the eqns. (10)–(12), together with $\bar{V}(NH_4ClO_4) = 23$ $cm^3\ mol^{-1}$, gives the satisfactory result:

$$\begin{aligned}& \bar{V}([Co(NH_3)_5X]\cdot(ClO_4)_2 \simeq \\ & \qquad \bar{V}([Co(NH_3)_5(NH_2)]\cdot(X)(ClO_4)) \qquad (13)\end{aligned}$$

The calculated difference is 3 $cm^3\ mol^{-1}$, well within the accuracy of the approximations. The equality for the fully ion-paired complexes of the same charge type is reasonable.

Summarizing, the activation volumes obtained fit satisfactorily in the existing picture of volume relations for cobalt(III) complexes.

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