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Volumes of Activation for the Linkage Isomerization Reaction of Thiocyanatopentaamminecobalt(III) Ion in Aqueous Solution and in Dimethylsulphoxide

D. A. PALMER, R. VAN ELDIK* and H. KELM**

Institute for Physical Chemistry, University of Frankfurt, Robert-Mayer Str. 11, D-6000-Frankfurt am Main-1, BDR

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Pressure and temperature dependencies of the rate of linkage isomerization of $Co(NH_3)_5SCN^{2+}$ *in acidic aqueous solution yielded the activation parameters:* $\Delta H^{\ddagger} = 102.8 \pm 0.8$ *kJ* mol^{-1}; $\Delta S^{\ddagger} = -14 \pm 3$ *J* K^{-1} mol^{-1}; $\Delta V^{\ddagger}_{exp} = -5.3 \pm 0.8$ cm^3 mol^{-1}. *A similar study in DMSO resulted in the following parameters:* $\Delta H^{\ddagger} = 105 \pm 2$ *kJ* mol^{-1}; $\Delta S^{\ddagger} = -2 \pm 4$ *J* K^{-1} mol^{-1}; $\Delta V^{\ddagger}_{exp} = -1.0 \pm 1.2$ cm^3 mol^{-1}. *These values emphasize that the rearrangements are intramolecular. They exclude the possibility that an "intimate ion-pair" is involved and rather suggest that the reactions proceed* via *a labile intermediate in which cobalt is bound to thiocyanate through a filled* π *orbital.*

Introduction

This paper represents a continuation of studies [1–4] made in this laboratory devoted to the effects of pressure (0–2 kbar) on reaction rates of coordination compounds with the aim of establishing the volume of activation, $\Delta V^{\ddagger}_{exp}$, as an additional tool in the diagnosis of the mechanisms involved.

A recent investigation [5] of the effect of pressure on the linkage isomerization of the nitrito ligand in $M(NH_3)_5ONO^{2+}$ in slightly acidic aqueous media, where M = Co(III), Rh(III) and Ir(III), confirmed that these reactions are intramolecular in nature. Earlier ligand exchange experiments [6] involving the Co(III) complex had shown that no exchange occurred between free NO_2^- and coordinated –ONO within the time range required for complete isomerization, clearly showing that the isomerization mechanism could not be intermolecular. In addition, measurements of the partial molar volumes of both isomers [5] allowed the construction of a volume profile diagram which gave further insight into the configuration or the transition state.

The rate of isomerization of $Co(NH_3)_5SCN^{2+}$ has been measured [7] in aqueous solution. The absence of thiocyanate exchange (<2%) proves that isomerization does not involve the dissociation of SCN^-. The authors discuss the rearrangement of the SCN ligand as involving either a labile intermediate in which cobalt is bound to both N and S, or an "intimate ion-pair", similar in form to that proposed by Sutin and coworkers [8, 9] for the hydrolysis of $Cr(SCN)(aq)^{2+}$ and, more recently [10], for the linkage isomerization of $Cr(SCN)(NCS)(aq)^{+}$. As increasing the ionic strength did not lead to an increase in the amount of SCN^- liberated during isomerization, the former mechanism was favoured [7]. By using protic and aprotic solvents, together with high pressure kinetics, we hoped to be able to further differentiate between the possible mechanisms.

Experimental

Materials

$[Co(NH_3)_5SCN]Cl_2 \cdot 1.5H_2O$ was synthesized and then separated from the isothiocyanato-isomer by ion-exchange chromatography, followed by repeated recrystallization [7, 11]. However the recrystallization procedure to remove the less soluble N-bonded isomer is tedious and also results in a considerable loss of product. This method was therefore modified by adding perchloric acid to the concentrated mother liquor obtained from the ion-exchange column. The ice-cold mixture was then filtered. The resulting crystals were stirred in a minimum amount of methanol and the residue filtered off. The perchlorate salt of the thiocyanato complex dissolves in methanol, whereas the isothiocyanato complex and traces of the parent aquo complex, do not. Cooling the solution to *ca.* –30 °C produced fine violet needles of $[Co(NH_3)_5SCN](ClO_4)_2$. These were recrystallized once from methanol, washed with ether and vacuum dried. The purified compound was stored in the dark at –30 °C. Calcd. for $[Co(NH_3)_5SCN](ClO_4)_2$: C, 3.0; H, 3.8; N, 20.9; S, 8.0. Found: C, 2.7; H, 3.5; N, 20.3; S, 7.8%.

The composition of $[Co(NH_3)_5NCS](ClO_4)_2$ [12], $[Co(NH_3)_5OH_2](ClO_4)_3$ [13] and $[Co(NH_3)_5DMSO](ClO_4)_3 \cdot 2H_2O$ [14] were also confirmed by microanalysis [15]. The characterization and purity

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*On leave from the Department of Chemistry, Potchefstroom University, Potchefstroom, South Africa.

**To whom correspondence should be addressed.

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of these complexes were checked by comparing their visible spectra, and in the case of the linkage isomers, their infra-red spectra, with those reported in the literature [7, 14, 16].

The remaining materials used in this work were of reagent grade. The solvent water was passed through an ion-exchange column, then doubly distilled. DMSO (Merck, <0.2% H_2O) was vacuum distilled from 4A molecular sieves [17].

Kinetic Measurements

All runs were monitored spectrophotometrically at 290 nm. A conventional sampling technique was used to follow the rate of isomerization in aqueous solution. The corresponding high pressure equipment has been described elsewhere [18]. Kinetic runs in DMSO were carried out "in situ" in a thermostatted high pressure cell [19] seated in a Zeiss DMR 10 spectrophotometer. The temperature was always controlled to within ±0.05 °C.

The reactions in aqueous solution were conducted at a hydrogen ion concentration of 10^{-3} *M* ($HClO_4$) and a complex concentration of 5×10^{-5} *M*, while the overall ionic strength was maintained at 0.1 *M* using $NaClO_4$. For the reactions in DMSO no acid was added, although the same complex concentration and ionic strength ($KClO_4$) were maintained.

In preliminary runs, in which the entire UV and visible spectrum was scanned, isosbestic points were observed during the first two half-lives at 548, 423 and 388 nm which correspond to a mixture of the two isomers. However at longer reaction times a slight shift (*ca.* 2 nm) in the isosbestic points was observed with the result that the final spectrum (*i.e.* taken after ten half-lives) did not correspond to pure $Co(NH_3)_5NCS^{2+}$. This observation is ascribed to the partial formation of solvolysis products, $Co(NH_3)_5OH_2^{3+}$ and $Co(NH_3)_5DMSO^{3+}$, depending on the solvent.

The observed first-order rate constants, k_{obs}, were obtained from the usual $\ln(A_t - A_\infty)$ *versus* time plots, where A_t and A_∞ represent the respective absorbancies measured at time t and of the isothiocyanato species calculated on the assumption that the reaction goes to completion. These plots were generally linear for at least two half-lives, further indicating the absence of side reactions during this time. The k_{obs} values, given in Table I as a function of temperature and pressure, represent the average of two individual runs. The activation parameters were calculated in the usual way.

Density Measurements

A digital instrument (DMA 02, Anton Paar K.G.) was used to determine the apparent molar volume, ϕ_i, of the linkage isomers in water and DMSO. The temperature was regulated to within ±0.001 °C. The average densities of the respective solvents were 0.997094 and 1.095207 g cm^{-3} at 25 °C. Complex concentrations were investigated in the range 6.3 to 14.7×10^{-3} *M*. As no detectable dependence of the ϕ_i values on concentration was found, the partial molar volumes of the complexes were assumed to be equal to the mean ϕ_i value under these conditions. A similar assumption was made in previous work [4].

TABLE I. Observed First-Order Rate Constants for the Linkage Isomerization of $Co(NH_3)_5SCN^{2+}$ at $\mu = 0.1$ *M*.

Solvent	Temperature °C	Pressure bar	10^5 k_{obs}[a] sec^{-1}
H_2O	50.0	1	3.08
	50.0	250	3.30
	50.0	500	3.23
	50.0	750	3.61
	50.0	1000	3.67
	50.0	1250	3.96
	50.0	1500	4.16
	35.5	1	0.475
	42.0	1	1.13
	58.0	1	7.65
	63.0	1	14.4
DMSO	50.0	1	7.59
	50.0	250	7.87
	50.0	500	7.80
	50.0	750	7.45
	50.0	1000	7.80
	50.0	1250	8.01
	50.0	1500	7.52
	41.4	1	2.53
	45.5	1	4.42
	55.7	1	15.3
	60.2	1	25.5

[a] Mean error of *ca.* 3%.

Results

An extrapolation of the k_{obs} values in Table I gives rise to a rate constant at 25 °C of 1.11×10^{-6} sec^{-1} in aqueous solution, which is in reasonable agreement with the reported value [7] of 8.0×10^{-7} sec^{-1} at 25 °C and $\mu = 1.1$ *M*.

No curvature of the $\ln k_{obs}$ *versus* pressure plots could be detected within the experimental error limits. The rate constants, $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta V^\ddagger_{exp}$ values are given in Table II.

The partial molar volumes of the complex cations in aqueous solution were estimated on the assumption [20] that $\bar{V}^\circ(H^+) = -4.5$ cm^3 mol^{-1}. Although the separation of the partial molar volume into its ionic components is more difficult in non-aqueous solvents, Parker *et al.* [21] have proposed that the molar volume change on transfer of Ph_4As^+ from a reference solvent (H_2O) to a given solvent

TABLE II. Activation Parameters for the Linkage Isomerization of $Co(NH_3)_5SCN^{2+}$ at $\mu = 0.1$ *M* at 50 °C.

Solvent	10^5 k_{obs} sec^{-1}	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J K^{-1} mol^{-1}	$\Delta V^{\ddagger}_{exp}$ cm^3 mol^{-1}
H_2O	3.06 ± 0.08	102.8 ± 0.8	−14 ± 3	−5.3 ± 0.8
DMSO	7.6 ± 0.4	105 ± 2	−2 ± 4	−1.0 ± 1.2

TABLE III. Partial Molar Volumes of the Linkage Isomers at 25 °C.[a]

Solvent	H_2O	DMSO
Complex Species	$\bar{V}^{o}$ cm^3 mol^{-1}	
$[Co(NH_3)_5SCN](ClO_4)_2$	194.0 ± 1.0	194.0 ± 2.3
$Co(NH_3)_5SCN^{2+}$	92.6	92.6
$[Co(NH_3)_5NCS](ClO_4)_2$	193.5 ± 0.7	192.4 ± 1.5
$Co(NH_3)_5NCS^{2+}$	92.1	91.0

[a] No attempt was made to adjust the ionic strength of these solutions.

should equal the molar volume change on transfer of the Ph_4B^- anion. They found that for H_2O to DMSO, $\Delta\bar{V}^{o}_{TR}$ $(Ph_4B^-) = 0$. A similar $\Delta\bar{V}^{o}_{TR}$ could be envisaged for other large monovalent anions, such as ClO_4^-. Thus $\bar{V}^{o}$ (ClO_4^-) would be equal in DMSO and H_2O, *i.e.* 50.7 cm^3 mol^{-1} [4]. The complete volume data are summarized in Table III. It should be noted that the last assumption does not affect the interpretation of the kinetic data.

Discussion

In keeping with our previous approach [4, 5] to such systems, and in conjunction with the generally accepted fact that aquation reactions of cationic cobalt(III) complexes are dissociative in character [4, 12, 22], the volume data can initially be treated within the framework of a dissociative mechanism. It has been established [4] that in aqueous solution $\bar{V}^{o}\{Co(NH_3)_5^{3+}\} \cong \bar{V}^{o}\{Co(NH_3)_6^{3+}\} = 55.1 \pm 1.1$ cm^3 mol^{-1}. Thus from previous studies [4, 5], the following equation can be formulated [25].

$$\Delta V^{\ddagger}_{DIS} = \bar{V}^{o}\{Co(NH_3)_5^{3+}\} + \bar{V}^{o}\{SCN^-\} - \\ - \bar{V}^{o}\{Co(NH_3)_5SCN^{2+}\} \\ = 55.1 + 40.2 - 92.6 = \\ = +2.7 \pm 1.8 \text{ cm}^3 \text{ mol}^{-1}$$

This value is incompatible with the measured $\Delta V^{\ddagger}_{exp}$ value of -5.3 ± 0.8 cm^3 mol^{-1} and demonstrates that a dissociative-type mechanism does not prevail. This conclusion merely substantiates the existing ^{14}NCS exchange data [7].

The type of intramolecular rearrangement associated with the linkage isomerization of $Co(NH_3)_5$-ONO^{2+} was not thought [5] to involve significant changes in electrostriction. The experimental $\Delta V^{\ddagger}_{exp}$ of -6.7 ± 0.4 cm^3 mol^{-1} therefore results from changes in bond lengths and angles during the formation of the transition state. As the overall volume change of this reaction is -12.9 ± 1.5 cm^3 mol^{-1}, virtually twice $\Delta V^{\ddagger}_{exp}$, the transition state must lie in the center of the volume profile. This is consistent with a synchronous rearrangement of the relatively "flexible" NO_2 group. The S-bonded thiocyanate complex is believed [7] to have a bond angle around the sulphur atom of close to 90°, such that at least part of the volume decrease can be interpreted in a similar manner [6, 24, 25]. For the overall volume change of reaction this decrease is virtually compensated for by an increase in volume during the formation of the linearly bound isothiocyanate complex. Thus the $\Delta\bar{V}$ value, calculated from the partial molar volumes of the individual isomers (see Table III), is virtually zero, *i.e.* -0.5 ± 1.7 cm^3 mol^{-1}.

A more fruitful approach is to compare these results with those obtained using a non-protic solvent such as DMSO. As can be seen from Table II, the rate constants, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are very similar in both solvents. The slightly slower rate of isomerization in H_2O, stemming from the somewhat more negative $\Delta S^{\ddagger}$ value, may be the result of hydrogen bonding of H_2O molecules to the $-SCN$ ligand. However, differences in $\Delta S^{\ddagger}$ of only 12 ± 7 J K^{-1} mol^{-1} allow no definite conclusions to be drawn. In addition, in terms of volume effects, the assumptions as to the value of $\bar{V}^{o}(ClO_4^-)$ in DMSO notwithstanding, the data in Table III show that no detectable difference exists between the molar volumes of the corresponding isomers in H_2O and DMSO. This tends to indicate that H-bonding of these complexes in their *ground state* does not manifest itself in measurable increases in electrostriction in this case.

On the other hand, the similarity of these parameters does tend to show that the mechanism does not involve bond cleavage with the formation of an "intimate ion-pair" in the transition state. The existence of such a species would be associated with a large solvent effect with a substantially faster rate in DMSO due mainly to the lower solvation energy of anions in this solvent [26] and to the higher association constants found in DMSO compared to H_2O [27]. Buckingham *et al.* [7] stated that the lack of a significant ionic strength effect on the amount of SCN^- lost during isomerization was also not in accord with an "intimate ion-pair" mechanism.

More significant are the volumes of activation which clearly show that a difference in behaviour in the two solvents does exist. The values of $\Delta V^{\ddagger}_{exp}$ primarily consist of two contributions [3]: an intrinsic part, $\Delta V^{\ddagger}_{intr}$, due to changes in bond lengths and angles, and a solvation part, $\Delta V^{\ddagger}_{solv}$, resulting from changes in electrostriction. The experimental results appear more compatible with the formation of a labile intermediate in which the cobalt atom is bound to the thiocyanate ion through a filled π molecular orbital spread over the whole ligand, with possible supplementary back-bonding as proposed earlier [7]. Such a mechanism would be characterized by a small value of $\Delta V^{\ddagger}_{intr}$ due to bond deformation as mentioned earlier. The difference in $\Delta V^{\ddagger}_{exp}$ found between the two solvents must originate from differences in $\Delta V^{\ddagger}_{solv}$. The partial separation of charges accompanying this mechanism would lead to an increase in interaction between the solvent and the reaction center in the *transition state* and should be more pronounced in protic solvents due to specific hydrogen bonding interactions. This accounts for the more negative $\Delta V^{\ddagger}_{exp}$ value found in aqueous solution.

Thus, as postulated previously [7], the linkage isomerization of $Co(NH_3)_5SCN^{2+}$ in solution, and possibly the thermally induced rearrangement in the solid state [7], and the base hydrolysis of this complex [7] involve a similar π-bonded transition state.

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