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Activation Volumes for the Linkage Isomerization Reactions of Nitritopentaammine Complexes of Cobalt(III), Rhodium(III) and Iridium(III) in Aqueous Solution

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The pressure and temperature dependencies of the rates of linkage isomerization of the complexes, $M(NH_3)_5ONO^{2+}$, where M represents Co(III), Rh(III) and Ir(III), were measured in aqueous solution at an ionic strength of 0.1 M. The volumes of activation were found to be −6.7 ± 0.4, −7.4 ± 0.4 and −5.9 ± 0.6 cm^3 mol^{-1}, resp. Partial molar volumes of the nitrito- and nitro-pentaamminecobalt(III) cations were determined at 82.3 ± 1.4 and 69.4 ± 0.1 cm^3 mol^{-1}. The volume profile for this reaction indicates the mechanism to be intramolecular in agreement with previous work [1, 2].

Introduction

The linkage isomerization of the nitrito ligand [1] in $Co(NH_3)_5ONO^{2+}$ has been cited in many reviews on the kinetics of coordination compounds [3, 4] as a classic example of an intramolecular rearrangement. Basically the fact that this reaction is orders of magnitude faster than the corresponding aquation reaction and the absence of significant exchange between coordinated and free nitrite ion in solution have established the intramolecular mechanism. Moreover, the apparent similarity in the rate parameters for linkage isomerization reactions involving the analogous complexes of Rh(III) and Ir(III) lead to the conclusion [2] that they are also intramolecular in nature.

Now that extensive high pressure studies [5, 6] on the kinetics of aquation of pentaamminecobalt(III) complexes have established the use of volume profile diagrams to characterize a mechanism, the isomerization of $Co(NH_3)_5ONO^{2+}$ provides an ideal opportunity to test this approach.

An intramolecular reaction would not be expected to involve significant changes in electrostriction during the formation of the transition state so that $\Delta V^{\ddagger}_{exp}$ should only reflect atomic displacements within the substrate. In inorganic kinetics, where charged species are normally involved, the contribution of solvation changes to $\Delta V^{\ddagger}_{exp}$ generally outweighs the intrinsic contribution which is directly diagnostic of the mechanism.

Finally, if the intramolecular mechanism holds for the Rh(III) and Ir(III) complexes then $\Delta V^{\ddagger}_{exp}$ should be virtually independent of the nature of the central metal atom.

Experimental

The complexes: $[Co(NH_3)_5ONO](ClO_4)_2$ [1]; $[Rh(NH_3)_5ONO](ClO_4)_2$ [2]; $[Ir(NH_3)_5ONO](ClO_4)_2$ [2]; $[Co(NH_3)_5NO_2]Cl_2$ [7]; $[Rh(NH_3)_5NO_2](NO_3)_2$ [8]; $[Ir(NH_3)_5NO_2](NO_3)_2$ [8]; $[Rh(NH_3)_6](NO_3)_3$ [9]; $[Ir(NH_3)_6]Cl_3$ [10], were prepared by standard methods although for the nitrito complexes the methods were modified to obtain the perchlorate salts. These complexes were precipitated by adding dropwise 70% $HClO_4$, rather than HCl, to the reaction mixture [1, 2]. They were then dried for 30 minutes under vacuum over P_2O_5. The purity of the samples was checked by microanalysis and the isomers were characterized from their IR and visible/UV spectra [11–14].

The isomerizations were followed spectrophotometrically using a recording single beam Zeiss PMQII instrument constructed about a high pressure cell [15] thermostatted to within ±0.1 °C. The 1 cm quartz cuvette, seated inside the pressure vessel, has a cylindrical neck (tolerance of ±0.01 mm) containing a movable teflon stopper fitted with a Viton O-ring.

A number of test runs were conducted with $Co(NH_3)_5ONO^{2+}$ in which the high pressure cell was exposed to the light beam for only *ca.* 15 seconds every 15 minutes to obtain the necessary readings. The rate constants so obtained agreed, within experimental error, *ca.* 2%, with those obtained by

TABLE I. Rate Constants for the Linkage Isomerization of $M(NH_3)_5ONO^{2+}$ at $\mu = 0.1$ *M*.

M	P bar	T °C	10^5k sec^{-1}
Co	1	20	3.68 ± 0.05
	1	25	7.38 ± 0.07
	1	30	13.7 ± 0.3
	1	35	25.3 ± 0.3
	1	40	42.7 ± 1.6
	250	30	15.9 ± 0.3
	500	30	17.5 ± 0.5
	750	30	18.4 ± 0.4
	1000	30	20.2 ± 0.5
	1500	30	21.5 ± 0.4
	2000	30	23.9[a]
	2500	30	27.8[a]
Rh	1	10	17.5 ± 0.8
	1	15	37.7 ± 0.8
	1	20	62.4 ± 0.5
	1	25	103.6 ± 1.5
	250	20	62.9 ± 1.4
	500	20	72.4 ± 2.1
	750	20	76.5 ± 1.4
	1000	20	81.1 ± 1.6
	1250	20	89.9 ± 1.2
Ir	1	30	5.55 ± 0.25
	1	35	11.2 ± 0.5
	1	40	20.3 ± 0.3
	1	45	37.0 ± 0.8
	1	50	68.8 ± 1.1
	250	30	6.94 ± 0.17
	500	30	7.00 ± 0.27
	750	30	7.35 ± 0.22
	1000	30	7.85 ± 0.16
	1250	30	8.08 ± 0.09
	1500	30	8.10 ± 0.27

[a] Only a single run was conducted.

leaving the cell exposed to the light beam throughout the run. Therefore photocatalysis was considered insignificant and the latter method was used for the remainder of the study.

Trace amounts of $CoCl_2 \cdot 6H_2O$ were added to other test runs which were followed by repetitive scan on a Cary 15 spectrophotometer. Isosbestic points were observed at 370 and 292 nm as were found in the absence of Co(II). The rate constants were also compatible with the remaining values.

A digital density apparatus, DMA 02 (Anton Paar KG, Austria) was used to determine the partial molar volumes of the various complexes. The instrument was thermostatted at 25.000 ± 0.002 °C. The difficulties incurred in making such measurements, and the absence of a concentration dependence of the apparent molar volumes, have been discussed elsewhere [6].

Results and Discussion

The rate constants are shown in Table I as a function of temperature and pressure. These values were determined at an ionic strength of 0.1 *M* adjusted with $NaClO_4$. Plots of lnk versus pressure are linear yielding $\Delta V^{\ddagger}_{exp}$ values for the Co, Rh and Ir complexes of −6.7 ± 0.4, −7.4 ± 0.4 and −5.9 ± 0.6 cm^3 mol^{-1}, respectively. For the former complex the pressure range was extended to 2500 bar, however no curvature of the lnk plot was observed. Unless otherwise stated, each rate constant given in Table I represents the mean value of at least two individual runs.

As reported in the literature [1], the rate of isomerization of $Co(NH_3)_5ONO^{2+}$ is independent of the nitrite ion concentration. However it is slightly dependent on the ionic strength with the rate constants decreasing by *ca.* 15% over the range 0–1 *M* ($NaClO_4$).

The temperature dependencies were reinvestigated as the literature values [2] were based on rather limited data. A complete summary of the rate parameters is presented in Table II.

The partial molar volumes of the nitrito- and nitropentaammine, and hexaammine complexes are given in Table III. The partial ionic molar volumes were calculated on the assumption that $\bar{V}_{H^+} = -4.5$ cm^3 mol^{-1}. The partial molar volumes of the appropriate sodium and potassium salts were taken from the literature [16]. Unfortunately it was not possible to measure the $\bar{V}$ values of $Rh(NH_3)_5ONO^{2+}$ and $Ir(NH_3)_5ONO^{2+}$ due to the higher reactivity of the former complex and to the presence of trace impurities in the latter complex together with its low solubility.

It has been clearly demonstrated [1] that in solution oxygen-18 labelled nitrite ions do not exchange with coordinated nitrite during the course of the linkage isomerization of $Co(NH_3)_5ONO^{2+}$. This evidence alone eliminates the possibility that the isomerization process is intermolecular, whether it be an associative or dissociative mechanism.

However, as cobalt(III) complexes are generally accepted as reacting via a dissociative pathway [3], which has been confirmed by high pressure studies [5, 6], this mechanism should be investigated first when considering the activation volume data for the linkage isomerization of $Co(NH_3)_5ONO^{2+}$. From our previous work [6], the volume of the pentacoordinated transition state, $Co(NH_3)_5^{3+}$, derived from the volume equation for a limiting dissociative mechanism, is equal to 54.9 ± 0.9 cm^3 mol^{-1}. This value was confirmed from measurements of the partial molar volume of $Co(NH_3)_6^{3+}$ which amounted to 55.1 ± 1.1 cm^3 mol^{-1}. For the linkage isomerization reaction the volume equation takes the form shown in (1).

TABLE II. Rate Constants and Activation Parameters for the Linkage Isomerization of $M(NH_3)_5ONO^{2+}$.

M	10^5 k^a sec^{-1}	ΔH‡ kJ mol^{-1}	ΔS‡ J K^{-1} mol^{-1}	ΔH$^{‡\,b}$ kJ mol^{-1}	ΔS$^{‡\,b}$ J K^{-1} mol^{-1}
Co	7.38	91.6 ± 0.8	−17 ± 3	92	−21
Rh	104.	80.2 ± 2.1	−33 ± 7	76	−50
Ir	2.87	95.3 ± 1.3	−11 ± 4	80	−59

^{a}25.0 °C. ^{b}Ref. 2.

TABLE III. Partial Molar Volumes of the Complex Salts and Ions in Aqueous Solution at 25 °C.

Complex	$\bar{V}$ cm^3 mol^{-1}	Ion	$\bar{V}$ cm^3 mol^{-1}
$[Co(NH_3)_5ONO](ClO_4)_2$	183.7 ± 1.4	$Co(NH_3)_5ONO^{2+}$	82.3
$[Co(NH_3)_5NO_2](NO_3)_2$	136.0 ± 0.1	$Co(NH_3)_5NO_2^{2+}$	69.4
$[Rh(NH_3)_5NO_2](NO_3)_2$	155.9 ± 1.0	$Rh(NH_3)_5NO_2^{2+}$	89.3
$[Ir(NH_3)_5NO_2](ClO_4)_2$	187.0 ± 1.4	$Ir(NH_3)_5NO_2^{2+}$	85.6
$[Rh(NH_3)_6](NO_3)_3$	134.0 ± 1.0	$Rh(NH_3)_6^{3+}$	67.4
$[Ir(NH_3)_6]Cl_3$	137.7 ± 0.8	$Ir(NH_3)_6^{3+}$	72.4
$KClO_4$	55.2	ClO_4^-	50.7
KNO_3	37.8	NO_3^-	33.3
KCl	26.25	Cl^-	21.75
$NaNO_2$	25.0	NO_2^-	30.9

$$Co(NH_3)_5ONO^{2+} \longrightarrow [Co(NH_3)_5^{3+} + NO_2^-]^{‡} \longrightarrow Co(NH_3)_5NO_2^{2+}$$

involving the volumes

$$\bar{V}_{RO} \qquad \Delta V^{‡}_{exp} \qquad \bar{V}_{R} \qquad \bar{V}_{NO_2^-} \qquad \bar{V}_{RN}$$

then

$$\bar{V}_R = \bar{V}_{RO} + \Delta V^{‡}_{exp} - \bar{V}_{NO_2^-} = 82.3 - 6.7 - 30.9 = 44.7 \pm 2.3 \text{ cm}^3 \text{ mol}^{-1} \qquad (1)$$

Obviously this value for $\bar{V}_R$ lies well outside the error limits for the established volume of $Co(NH_3)_5^{3+}$ and is sufficient ground to reject the dissociative mechanism.

Therefore we are left with the intramolecular mechanism. Here a consideration of the entire volume profile diagram is necessary. The overall volume change, $\Delta\bar{V}$, is equivalent to $(\bar{V}_{RN} - \bar{V}_{RO}) = -12.9 \pm 1.5$ cm^3 mol^{-1}. In other words, the transition state lies virtually in the center of the profile as shown in Figure 1 and is entirely consistent with the type of synchronous rearrangement envisaged by Basolo *et al.* [3].

On the basis of the similarity between the rate constants and activation parameters, ΔH‡ and ΔS‡, for the linkage isomerizations of the Co, Rh and Ir nitrito complexes it was concluded [2] that all react via the same mechanism. In fact the Rh complex reacts approximately 36 times faster than the Ir

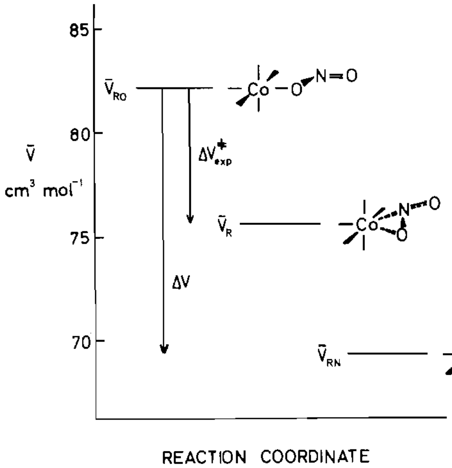

Figure 1. Volume profile diagram for the linkage isomerization of $Co(NH_3)_5ONO^{2+}$.

analog and 14 times faster than Co. A brief survey of the results summarized in Table II shows this to be due to the lower $\Delta H^{\ddagger}$ for Rh. However the $\Delta S^{\ddagger}$ are comparable and somewhat negative which is also consistent with increased bonding, or a chelated "nitrito" group, in the transition state.

The volumes of activation are also virtually identical within experimental error, compounding the evidence for a common mechanism.

Despite the lack of values for $\bar{V}_{RO}$ for $Rh(NH_3)_5ONO^{2+}$ and $Ir(NH_3)_5ONO^{2+}$ the volume equation treatment can be applied by assuming that the $\Delta\bar{V}$ values for all three reactions are identical, *i.e.* −13 cm^3 mol^{-1}. Utilizing equation (1) ultimately leads to values for $\bar{V}_R$ for the hypothetical transition state of 63.9 ± 2.8 and 61.7 ± 3.5 cm^3 mol^{-1}, respectively. The measured partial molar volumes given in Table III for the Rh and Ir hexaammine cations are 67.4 ± 1.0 and 72.4 ± 0.8 cm^3 mol^{-1}. Here again the volume data is not in keeping with a dissociative mechanism.

Acknowledgements

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