

KINETIC STUDY OF THE LINKAGE
ISOMERISM IN $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{X}_2$
($\text{X}=\text{Cl}^-, \text{Br}^-, \text{I}^-$) IN THE SOLID
STATE IN KBr DISCS.

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ABSTRACT

The nitrito \rightarrow nitro isomerization in nitritopentaamminecobalt(III) halides has been known. In this paper, the effect of the size of the counter ions (noncoordinated groups) on the rate of isomerization in nitritopentaamminecobalt(III) halides, is reported. The rate of isomerization is decreased by increasing the size of the counter ions. This decrease is explained on the basis of steric interaction between the nitro groups in the inner sphere and the counter ions in the outer sphere of these complexes.

INTRODUCTION

Kinetic studies of linkage isomerism in $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ both in the solid state and in aqueous solution have been reported by Adell (1). In both cases the reaction was followed spectrophotometrically in solution in the visible region. He found that the reverse reaction could be initiated by allowing $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$ to stand in sunlight

for a long period of time. Wendlandt and Woodlock (2) have reported that a nitro \rightarrow nitrito transition was induced on the complexes, $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^- \text{X}_2$ ($\text{X}=\text{Cl}^-, \text{Br}^-, \text{I}^-, \text{NO}_3^-$), by ultraviolet irradiation. For example, the curve peak maximum in the reflectance spectrum of a sample of $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$, shifted from 455 nm to 475 nm after two one minute interval irradiations by ultraviolet lamp. It is known (3,4) that the nitrito form in $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ has a strong absorption at 1060 cm^{-1} in the IR region whereas the pure nitro form does not absorb at this wavelength. Beattie and Satchell (5) have used the change of the intensity of this absorption band to study the isomerization of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ in the solid state in KCl discs and found that it is essentially an equilibrium process. This isomerization has also been studied by differential thermal techniques (6) and the value of $24.04 \pm 1.03 \text{ kcal mole}^{-1}$ was reported for the activation energy of the reaction. Isomerization of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$ either in solution (7) or in the solid state (5) follows a first order kinetics.

One point of interest in connection with the linkage isomerism is the steric effects of the counter ions (noncoordinated group) and ligands (in the coordination sphere of the central metal ions). However, limited information is available con-

cerning the steric effects of the counter ions on the isomerization process (8).

In this article the isomerization of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{X}_2$ ($\text{X}=\text{Cl}^-, \text{Br}^-, \text{I}^-$) complexes have been studied in KBr discs to evaluate the effect of the increase in the size of the counter ions on the rates of the isomerization.

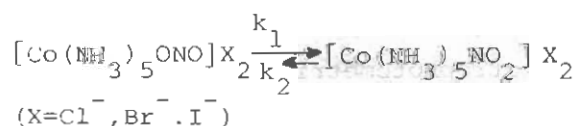
EXPERIMENTAL

The nitro and nitritopentaamine cobalt(III) chlorides, bromides and iodides have been prepared by the methods reported in the literature (9,10,2). In order to prepare the KBr discs, 20 grams of pure potassium bromide and 0.40 grams of the complex (a 1.96 weight percent mixture) were ball milled at an average speed for 3 hours to obtain a homogeneous powder. A sample (0.21 grams) of this powder was pressed under vacuum using a pressure of 19000 psi. Thickness of this KBr disc was 0.6mm. To minimize the error which could be caused by weighing of the samples and preparing the homogeneous mixture, for each of the complexes, only one disc was used in kinetic measurements. In order to repeat the kinetic measurements at various temperatures, after finishing a set of measurements at a fixed temperature the disc was placed in a desiccator covered with a glass plate (1.5mm thickness) and it was irradiated by a 366nm mercury lamp from a distance of 80mm for a

period of 2 hours to ensure a complete conversion of the nitro isomer into the nitrito isomer. Infrared spectra and qualitative analyses of the complexes indicated that they did not decompose by repeated UV irradiation of the samples. To study the kinetics of the reaction, the KBr disc was placed in a thermostated aluminium box with a lid. On removal from the box the disc was rapidly cooled to room temperature and infrared of the sample was taken only in the $1000-1100\text{cm}^{-1}$ range. It was assumed that negligible isomerization occurred during the time occupied by the infrared measurement. Complete spectra were taken only at the beginning and at the end of kinetic runs. Infrared spectra were recorded on a Perkin-Elmer Model 567 spectrophotometer. Optical densities were calculated using a base-line method (11) and all the slopes in the $\log (A_t - A_e)$ versus t and also $\log k$ versus $1/T$ diagrams were calculated by least squares method.

RESULTS AND DISCUSSION

Kinetic study of the following reversible reaction in KBr discs



was carried out by measuring the change in optical density of the nitrito peak at $1060, 1040$ and 1010cm^{-1}

for chloride, bromide and iodide respectively, against time using equation 1

$$\log(A_0 - A_e) - \log(A_t - A_e) = kt/2.303 \quad 1$$

$$(k = k_1 + k_2)$$

A plot of $\log(A_t - A_e)$ versus time (t) gave a straight line expected for a first order reaction. Rate constant of the reaction at a given temperature was calculated from the slope of this line. Optical densities of the complex at the time t and at the equilibrium are indicated by A_t and A_e respectively. In order to obtain A_e , the KBr disc of the complex was held at the temperature of the kinetic measurements for a long time until no further change in the optical density was observed. Since the rate constant (k) in an equilibrium process is equal to sum of the rate constants of the forward and the reverse reactions ($k_1 + k_2$) and the equilibrium constant is also equal to k_1/k_2 , separate values for k_1 and k_2 were obtained by calculating the equilibrium constant using equation 2.

$$K = \frac{A_0(\text{ONO}) - A_e(\text{ONO})}{A_e(\text{ONO})} \quad 2$$

$A_0(\text{ONO})$ in equation 2 was taken as the optical density of the nitrito complex at the beginning of the reaction (t=0). In order to obtain the $A_0(\text{ONO})$ the nitro complex was irradiated with a 366nm mercury lamp for 2 hours for a complete conversion

to occur. Kinetic measurements were carried out at 324, 330, 337.5 and 345.5 degrees Kelvin (Table I) and $\log(A_t - A_e)$ versus t plots for the nitritopentaammine cobalt(III) halides at 324 and 345.5 K as specimen, are given in Figs. 1 and 2. The relationship between $\log k$ and the reciprocal of the absolute temperature is also shown in Fig. 3. From this graph, the thermodynamic quantities of activation were calculated (Table II).

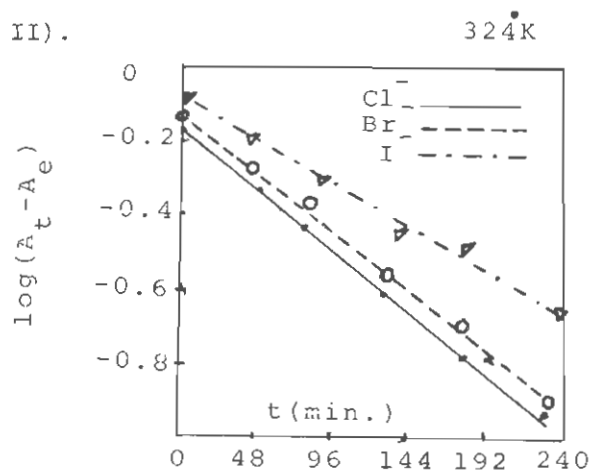


Fig.1 First order relationships for isomerization of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{X}_2$ at 324 K.

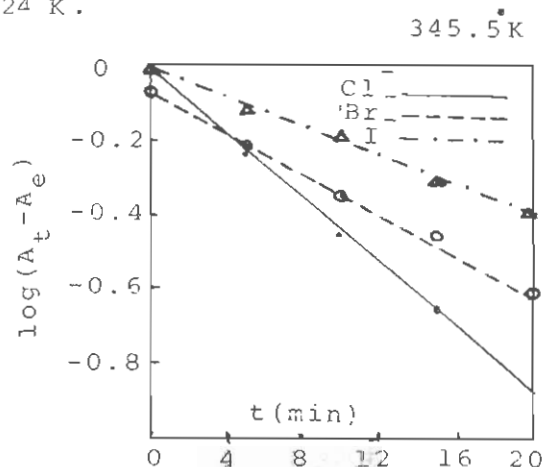


Fig.2 First order relationships for isomerization of $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{X}_2$ at 345.5 K.

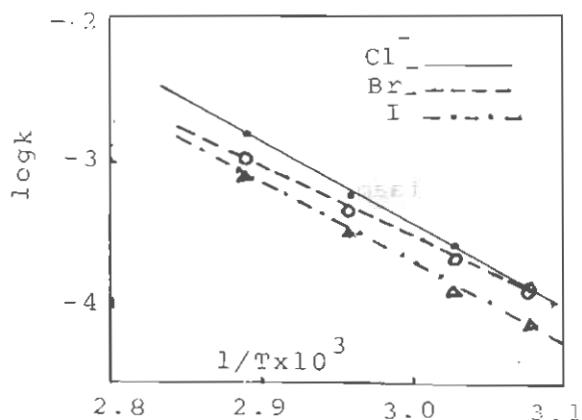
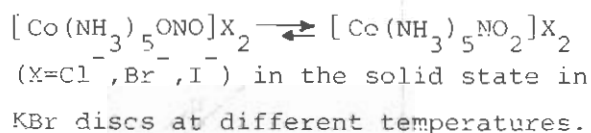


Fig.3 The relationship between log k and the reciprocal of the absolute temperature.

Table(I) Rate constants for the isomerization reaction



T(°K)	[Co(NH ₃) ₅ ONO]Cl ₂		[Co(NH ₃) ₅ ONO]Br ₂		[Co(NH ₃) ₅ ONO]I ₂	
	k × 10 ⁴ sec ⁻¹	k ₁ × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹	k ₁ × 10 ⁴ sec ⁻¹	k × 10 ⁴ sec ⁻¹	k ₁ × 10 ⁴ sec ⁻¹
324	1.37	1.17	1.30	1.03	0.83	0.54
330	2.71	2.35	2.28	1.85	1.31	0.95
337.5	6.03	5.22	4.40	3.88	2.46	1.93
345.5	14.9	12.8	10.51	9.26	7.36	5.71

Table (II) Thermodynamic quantities of activation for isomerization of [Co(NH₃)₅ONO]X₂ (X=Cl⁻, Br⁻, I⁻) in the solid state in KBr discs.

Complex	ΔH [‡] k Cal mol ⁻¹	ΔS [‡] Cal deg ⁻¹ mol ⁻¹	ΔG [‡] k Cal mol ⁻¹
Cl ⁻	24.02±0.01	-2.06	24.64±0.01
Br ⁻	20.94±0.01	-11.68	24.42±0.01
I ⁻	21.78±0.01	-10.57	24.93±0.01

ΔS[‡] and ΔG[‡] values are calculated for T=298°K.

The data in Table (I) indicate that the rate of isomerization of the

nitrito complexes at each temperature, is consecutively decreased from the chloride to the iodide.

Considering the fact that the cone angle of a nitro group(M-NO₂) is larger than that of a nitrito group(M-ONO), we should expect a greater steric interaction to exist in the packed KBr disc between the nitro group in the coordination sphere and

the larger counter ions, and therefore the reaction rates should fall in the order: [Co(NH₃)₅ONO]Cl₂ > [Co(NH₃)₅ONO]Br₂ > [Co(NH₃)₅ONO]I₂

The same order is also borne out by the gain in LFSE, going from the nitrito to the nitro isomer (Table III). This gain in energy is calculated from the absorption maxima of the nitrito and nitro forms in KBr discs taken by a Cary 17D spectrophotometer.

Table(III) absorption maxima of [Co(NH₃)₅ONO]X₂ and [Co(NH₃)₅NO₂]X₂ complexes in the solid state in KBr disc (in cm⁻¹ for ¹A_{1g} → ¹T_{1g} transition).

X	[Co(NH ₃) ₅ ONO]X ₂	[Co(NH ₃) ₅ NO ₂]X ₂	gain in LFSE
Cl ⁻	20000	24390	4390
Br ⁻	19608	23529	3921
I ⁻	19230	21277	2047

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