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THE KINETIC STUDY OF THE LINKAGE ISOMERISM IN $[Co(NH_3)_5NO_2]F_2$ COMPLEX

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Abstract

In this research project, the nitrito $\rightleftharpoons$ nitro isomerization of $[Co(NH_3)_5NO_2]F_2$ complex has been studied. Isomerization of this complex in the solid state follows a first order kinetics. The rate of isomerization at different temperatures was determined using a Fourier Transform Infrared Spectrophotometer. $\Delta S^{\neq}$ and $\Delta G^{\neq}$ are calculated at 298 K. The infrared, visible and ultraviolet spectra of this compound are also reported.

Introduction

An extensive investigation of the nitrito $\rightarrow$ nitro isomerization was made by Adell [1]. The rates of rearrangement were determined spectrophotometrically. Measurements were made on the solid state and aqueous solution, in all cases the data were found to give a first-order plot. The isomerization in solution is ten to one hundred times faster than in the solid state. This can only be approximate because the rate of isomerization of the solid depends on the anion portion of the salt. For example, Adell calculated the rate constant of rearrangement of $[Co(NH_3)_5ONO]X_2$ where $X=Cl^-, I^-$ and NO_3^-, and showed it to be different. Phillips, Chol, and Larrabee studied the kinetics of the following reaction in the solid state and solution [2]:

$$[Co(NH_3)_5ONO]Cl_2 \rightleftharpoons [Co(NH_3)_5NO_2]Cl_2$$

In their study they used FT-IR in the solid state and visible spectrum in the solution. Heravi and Abedini have studied the effect of the size of the counter ions (non coordinated groups) on the rate of isomerization in nitrito pentaammine cobalt (III) halides (Cl^-, Br^-, I^-) [3].

In this article, the kinetic study of the linkage isomerism in $[Co(NH_3)_5NO_2]F_2$ is reported. In the IR region, the nitrito group in $[Co(NH_3)_5ONO]F_2$ has a strong absorption band at 1057 cm^{-1} whereas the pure nitro complex does not show any band in this region. The change of the intensity of this absorption band was used to study the isomerization of $[Co(NH_3)_5ONO]F_2$ in the solid state in KBr pellet.

Keywords: Kinetic linkage isomerization; Cobalt complexes

Experimental Section

Elemental analyses were performed with an Elemental Analyzer CHN-O-RAPID, Heraeus and an Atomic Absorption, 2830, Perkin-Elmer. Infrared spectra were obtained on an FT-IR Spectrophotometer, IFS88, Bruker (KBr pellet). UV/VIS spectrum was obtained on a UV/VIS/NIR Spectrophotometer, Lambda 9, Perkin-Elmer.

Preparation

$[Co(NH_3)_5Cl]Cl_2$ and $[Co(NH_3)_5ONO]Cl_2$ were prepared by the methods reported in the literature [4,5]. $[Co(NH_3)_5NO_2]F_2$ was prepared by adding AgF to $[Co(NH_3)_5NO_2]Cl_2$ [6].

Infrared Spectra of Nitro and Nitrito Complexes

The stretching vibration and degenerate deformation of the NH_3 group appeared at 3280 and 1311 cm^{-1} respectively. The presence of a band at 1427 cm^{-1} could be assigned to the asymmetric stretching of the nitro group (in nitrito form, instead of this band, there are two bands at 1057 and 1453 cm^{-1} that belong to the symmetric stretching and asymmetric stretching of the nitrito group respec-

tively). The wagging vibration of NO_2 appears at 596 cm^{-1} (this band does not appear in the IR spectrum of nitrito form). Presumably, a band at 445 cm^{-1} region belongs to Co-N stretching vibration [7].

Electronic Spectrum of Nitro Complex

In the electronic spectrum three bands were observed. The first and the second band could be assigned to the following spin allowed d-d transitions:

$^1A_{1g} \rightarrow {}^1T_{1g}$ 21872 cm^{-1} ($\varepsilon_{max} \simeq 55$)

$^1A_{1g} \rightarrow {}^1T_{2g}$ 30703 cm^{-1} ($\varepsilon_{max} \simeq 1300$)

but the second transition could be obscured by charge transfer because of high intensity. The third absorption was observed at 41667 cm^{-1} ($\varepsilon_{max} \simeq 10000$) which is assigned to charge transfer.

Kinetic Study

The kinetic study of the isomerization of nitrito $\rightleftharpoons$ nitro was carried out by measuring the change in absorbance[1] of nitrito peak at 1057 cm^{-1} against time.[2] Therefore, after preparation of KBr pellet of $[Co(NH_3)_5NO_2]F_2$ it was irradiated by a 336nm UV lamp from a distance of 80mm for 2 hours to ensure a complete conversion of the nitro isomer into the nitrito isomer. The IR spectrum of the sample was then taken at 298k and during isomerization (for several times) and finally spectrum taking was repeated at the equilibrium.

Kinetic measurements were repeated at 313, 323, 335K to calculate the $\Delta S^{\neq}$ and $\Delta G^{\neq}$ of isomerization. During the isomerization, the KBr disc was placed in a thermostated aluminium box with some calcium chloride powder in the bottom. The isomerization during the time of taking the IR spectra was negligible.

Figure 1 shows the IR spectra of $[Co(NH_3)_5ONO]F_2$ in 323K at t=0, 120, 280 minutes and equilibrium.

Results and Discussion

The complex of $[Co(NH_3)_5NO_2]F_2$ was changed to $[Co(NH_3)_5ONO]F_2$ by UV irradiation with a 366 nm wavelength, and after a period of time the $[Co(NH_3)_5ONO]F_2$ reached an equilibrium with $[Co(NH_3)_5NO_2]F_2$. The reaction is as follows:

$$[Co(NH_3)_5ONO]F_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Co(NH_3)_5NO_2]F_2$$

The kinetic study of this isomerization was carried out in solid state by measuring the change in the infrared absorption peak at 1057cm^{-1} which is due to the symmetric

[1] The absorbances were calculated by base line method.

[2] All slopes of the plots were calculated by least squares method.

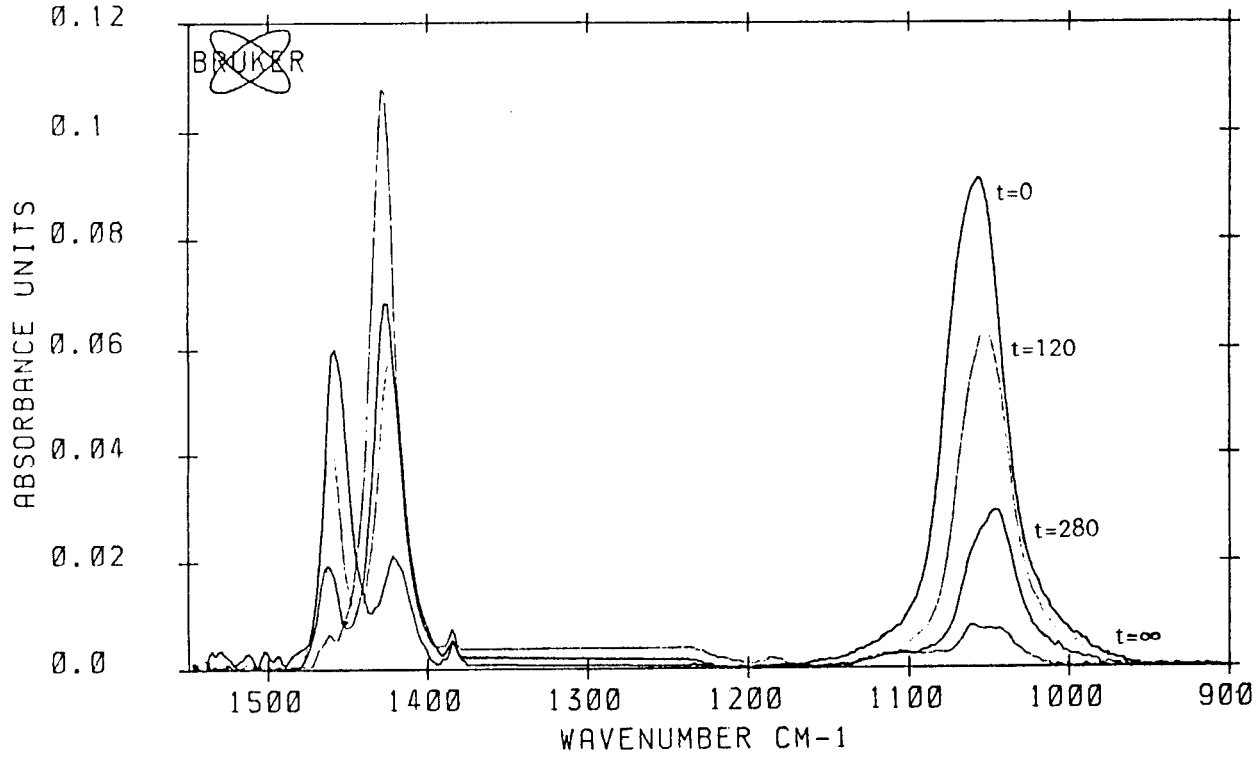

Fig. 1. Infrared spectra of KBr pellet of $[Co(NH_3)_5ONO]F_2$ at 323K. Times are in minutes.

stretching vibration of the nitrito group. Starting with 100% nitrito isomer, the following equation can be used [8]:

$$2.3 \log \frac{A_o - Ae}{A_t - A_e} = kt = (k_1 + k_2)\, t \qquad (1)$$

where A_t, A_e and A_o are the absorbance of the nitrito complex at 1057 cm^{-1} at time t, equilibrium (infinite time) and t=0, respectively. Nitrito isomer (100%) was obtained by irradiation of nitro isomer by using UV (366 nm) for 2 hours.

A plot of log $(A_t - A_e)$ versus time (t) gave a straight line (which was expected for a first order reaction) with a slope of $-(k_1 + k_2)/2.3$. This plot at 323K is shown in Fig 2. By using the slope of this plot $-(k_1 + k_2)/2.3$ and calculating the equilibrium constant ($K = \frac{k_1}{k_2}$) from equation 2, k_1 and k_2 can be determined.

$$K = \frac{k_1}{k_2} = \frac{A_{o\,(ONO)} - A_{e\,(ONO)}}{A_{e\,(ONO)}} \qquad (2)$$

$A_{o(ONO)}$ in equation (2) is the absorbance of nitrito complex at the 1057 cm^{-1} region at the beginning of the reaction (t=0). The measurements were carried out at 313, 323 and 335K.

On the basis of the following equation [9], the plot of log k

$$\log k^* = -\frac{E_a}{2.303\,R}\frac{1}{T} + \log A^{**} \qquad (3)$$

versus 1/T gave a straight line (Fig 3) with a slope of $\frac{-E_a}{2.303\,R}$ and an intercept of log A, where A is the frequency factor. By using the slope and intercept values, $\Delta S^{\neq}$ and $\Delta G^{\neq}$ of isomerization were obtained (Table 1).

The electronic spectra of the complexes such as $[Co(en)_3]^{3+}$, $[Co(en)_2(NH_3)_2]^{3+}$ are very similar to the octahedral ammonia complex [10] i.e., $[Co(NH_3)_6]^{3+}$. In effect, the intensities and apparent splitting patterns from the absorption spectra reflect the essentially octahedral $[M(NH_3)_6]^{3+}$ chromophore. Similar spectrum could be

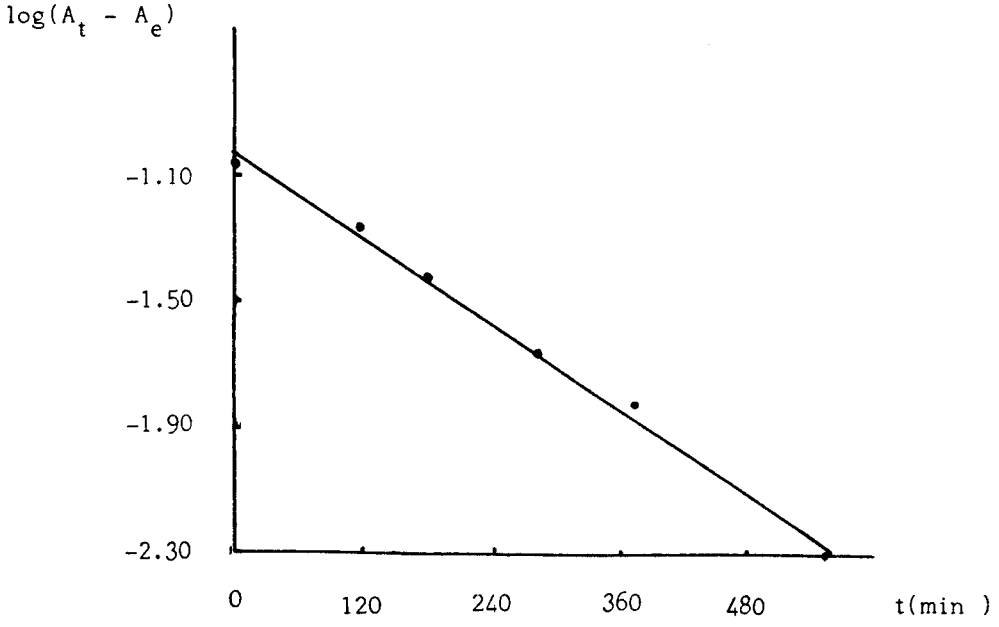

Fig. 2. The plot of log $(A_t - A_e)$ versus time(t) at 323K which indicates the first order relationships for isomerization of $[Co(NH_3)_5ONO]F_2$.

Table 1. Thermodynamic quantities of activation for isomerization of $[Co(NH_3)_5ONO]F_2$ in the solid state in KBr pellet (at 298K)

$\Delta H^{\neq}$ (kcal mol^{-1})	$\Delta S^{\neq}$ (cal $deg^{-1} mol^{-1}$)	$\Delta G^{\neq}$ (kcal mol^{-1})
19.54	-8.64	22.12

* On the basis of equation (1) $k = k_1 + k_2$

** $A = \frac{k' T}{h} e^{\Delta S^{\neq}/R}$

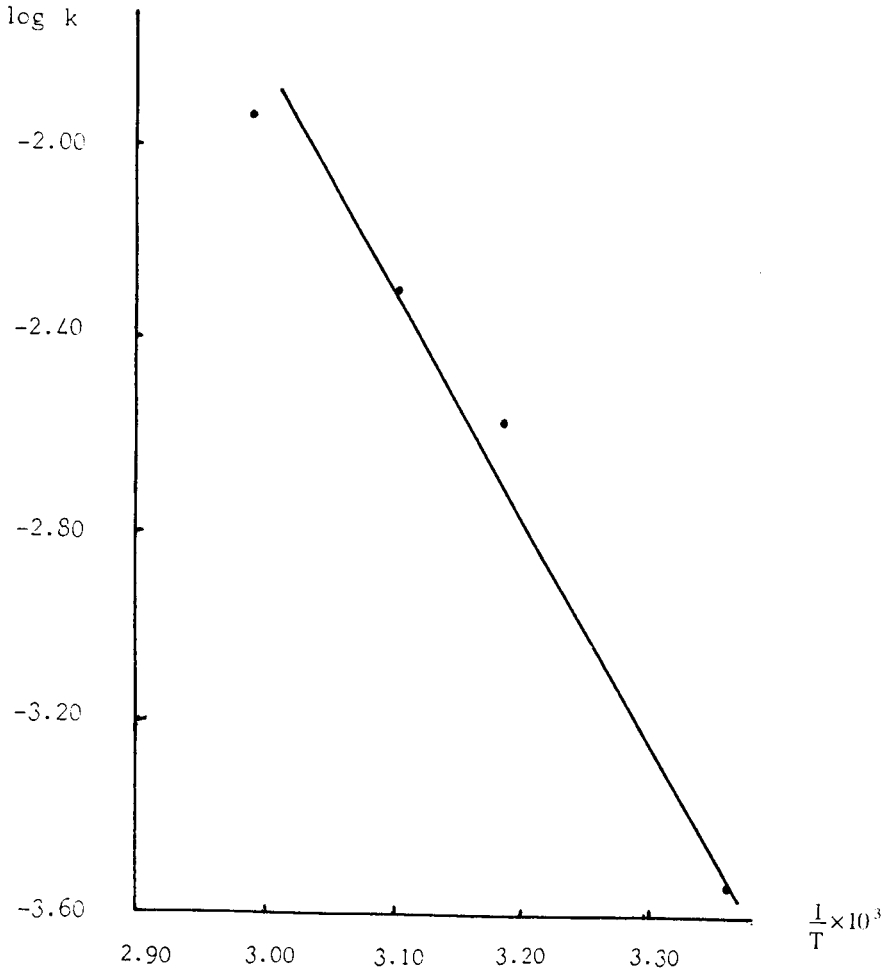

Fig. 3. The plot of log k versus $\frac{1}{T}$ (the reciprocal of the absolute temperature).

expected for the $[Co(NH_3)_5NO_2]F_2$ complex. The electronic spectrum of this complex has three bands at 21872 ($\varepsilon_{max} \simeq 55$), 30703 ($\varepsilon_{max} \simeq 1300$) and 41667 cm^{-1} ($\varepsilon_{max} \simeq 10000$). The first band is assigned to $^1A_{1g} \longrightarrow {}^1T_{1g}$ that is similar to the first band of $[Co(NH_3)_6]^{3+}$, 21200 cm^{-1} ($\varepsilon_{max} \simeq 56$). The second d-d transition has to be observed at $\simeq$ 30000 cm^{-1} region, thus, could be obscured by the first charge transfer ($^1A_1 \longrightarrow {}^1B_1$), i.e., 30703 cm^{-1} band because of high intensity. The third band is assigned to the second charge transfer ($^1A_1 \longrightarrow {}^1B_2$).

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