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Thermochimica Acta 409 (2004) 189–193

thermochimica acta

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Thermoanalytical study of linkage isomerism in coordination compounds Part I. Reinvestigation of thermodynamic and thermokinetic of solid state interconversion of nitrito (ONO) and nitro (NO_2) isomers of pentaaminecobalt(III) chloride by means of DSC

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Received 1 May 2003; received in revised form 20 June 2003; accepted 24 June 2003

Abstract

Solid state thermal isomerization of $[Co(NH_3)_5(ONO)]Cl_2$ (nitrito isomer) to $[Co(NH_3)_5(NO_2)]Cl_2$ (nitro isomer) and reverse reaction were investigated by non-isothermal differential scanning calorimetry (DSC) and found to be essentially an equilibrium process. The interconversions are accelerated at above 65 °C and reach to equilibrium state at about 155 °C. After establishment of the equilibrium the relative amounts of two isomers at any temperature are governed by Gibbs free energy relationship. The experimental enthalpy changes of isomerization of pure nitrito and nitro solid samples to the equilibrium state are -4.67 (± 0.19) and 0.99 (± 0.05) $\mathrm{kJ\,mol^{-1}}$, respectively. From these values, total enthalpy change was calculated as: $\Delta H^\circ = -5.66(\pm 0.20)\,\mathrm{kJ\,mol^{-1}}$. Using Gibbs free energy relationship, equilibrium constant, total free energy and entropy changes were estimated at 60 °C as: $K = 7.72\,(\pm 0.8)$, $\Delta G^\circ = -5.54\,(\pm 0.20)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^\circ = -0.36\,(\pm 0.80)\,\mathrm{J\,K^{-1}\,mol^{-1}}$.

An initial rate method has been developed to determine the kinetic parameters of these reactions from non-isothermal DSC data. Both nitro to nitrito and reverse reactions obey first order kinetic law in solid state. Estimated activation parameters of forward and reverse paths at 60 °C are $\Delta H^{\ddagger}_{\mathrm{ONO}} = 103\,(\pm 3)\,\mathrm{kJ\,mol^{-1}}$, $\Delta S^{\ddagger}_{\mathrm{ONO}} = -6\,(\pm 1)\,\mathrm{J\,K^{-1}\,mol^{-1}}$, $\Delta H^{\ddagger}_{\mathrm{NO_2}} = 108(\pm 5)\,\mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\ddagger}_{\mathrm{NO_2}} = -3(\pm 1)\,\mathrm{J\,K^{-1}\,mol^{-1}}$, respectively. The negative activation entropy of both directions support the intramolecular mechanism of isomerization, including formation of a seven coordinate transition state, which formerly suggested based on spectral and X-ray methods.

Keywords: Cobalt(III) pentaamine complexes; Linkage isomers; Nitro and nitrito; DSC; Kinetic

1. Introduction

It is more than one century that linkage isomerism approach launched into coordination chemistry through preparation of nitro, $[Co(NH_3)_5(NO_2)]Cl_2$ and nitrito, $[Co(NH_3)_5(ONO)]Cl_2$ isomers of pentaamminecobalt(III) complex by Jorgensen in 1894.

During following decades, several spectral methods have been employed for exploration of mechanistic details of interconversion of these linkage isomers and identification of their relative stability, including IR [1–4], UV-Vis [5–7], NMR spectroscopies [8,9] and X-ray crystallography of powder and single crystal samples [10–13]. However, kinetic and thermodynamic of NO_2/ONO interconversion were rarely investigated by thermal methods [14]. From these investigations, it is clear that N-bonded nitro isomer is more stable than O-bonded nitrio and conversion of nitrito to nitro could occur simultaneously both in solution and solid state via an intramolecular mechanism and the reaction rate is accelerated at elevated temperature [5,6,15]. Also, It was found that nitro isomer could be photochemically converted to nitrito form upon irradiation of nitro isomer with UV lamp or sunlight in solid state [16].

Although there is considerable reports concerning spectral analysis of kinetic of isomerization reaction, the extent of thermal interconversion of nitro and nitrito isomers of pentaamminecobalt(III) complex has been subject of recent controversial reports. Someone considered the thermal conversion of nitrito to nitro isomer as a totally irreversible reaction [17], while other one treated this reaction as partially

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doi:10.1016/S0040-6031(03)00361-7

reversible [2,18]. X-ray crystallography results showed that interconversion of nitro and nitrito isomers of various salts of pentaamminecobalt(III) complex occur without significant phase transition in solid state [12,13], so that one can consider the amount of evolved or adsorbed heat as a criterion of chemical transformation through progress of thermal isomerization reaction (1).

$$[Co(NH_3)_5(ONO)]Cl_2 \rightleftarrows [Co(NH_3)_5(NO_2)]Cl_2 \quad (1)$$

The present work is aimed to resolve the reversibility of above reaction by means of differential scanning calorimetry (DSC) and to determine its thermodynamic parameters. The results obtained in the course of this study led to development of a simple and general method for determination of thermodynamic parameters of two components equilibrium reactions in solid state which are far from equilibration at ambient temperature. Beside thermodynamic investigation, DSC results may allow one to study kinetic of thermal phenomena. Thus, a further aim of this work is to determine the kinetic parameters of isomerization reaction (1).

2. Experimental procedure

$[Co(NH_3)_5(NO_2)]Cl_2$ and $[Co(NH_3)_5(ONO)]Cl_2$ were prepared and purified according to a published method [10]. Finely powdered samples of these compounds were obtained after washing them with ethanol and drying in air flow. The samples purity was checked by means of elemental analysis and IR spectra. In all experiments, a freshly purified sample was used and protected from light source. Differential scanning calorimetry experiments were carried out using a PL DSC-Gold calorimeter (Polymer Labs Ltd., UK). The DSC experiments were conducted non-isothermally at linear heating rate of 28 K min^{-1}. The cooling curve was obtained under air-cooled condition.

3. Results and discussion

3.1. Thermodynamic

Fig. 1 shows DSC curve of pure $[Co(NH_3)_5(ONO)]Cl_2$ in a wide temperature range. Several decomposition endothermic peaks are appeared after a small exothermic peak (shown in circle).

The initial, maximum and final temperatures of the latter in a representative experiment with heating rate of 28 °C min^{-1} are 64, 113 and 150 °C, respectively. This initial peak could be assigned to the thermal process associated with isomerization reaction (1). The identity of the species appeared after this process was investigated by means of IR spectra. The fundamental absorption bands of the complex framework were preserved, but relative intensity of nitrito (ONO) and nitro (NO_2) absorption bands were significantly changed. In order to examine the reversibility of isomerization reaction, thermal behavior of pure $[Co(NH_3)_5(NO_2)]Cl_2$ was studied. In this experiment, a more little endothermic peak appeared at same temperature range with initial, maximum and final temperatures of 89, 122, 151 °C, respectively. The isomerization peaks of both isomers are represented in Fig. 2. These observations may allow one to suppose that neither pure nitro nor pure nitrito is a completely thermodynamically stable state. In fact, both pure isomers could be considered as metastable states which convert to a stable state upon heating. Both isomers are involved in the stable state, in which relative amount of two isomers could be deduced from equilibration data. Scheme 1 shows the enthalpy relationship of two metastable and one stable states. $\Delta H_{ONO}^{exp.}$ and $\Delta H_{NO_2}^{exp.}$ are enthalpy changes of conversion of metastable pure nitrito and pure nitro states to equilibrium stable state, respectively. These parameters could be experimentally determined by means of integration of corresponding peak in the given temperature range. $\Delta H^{hypo.}$ is defined as enthalpy change

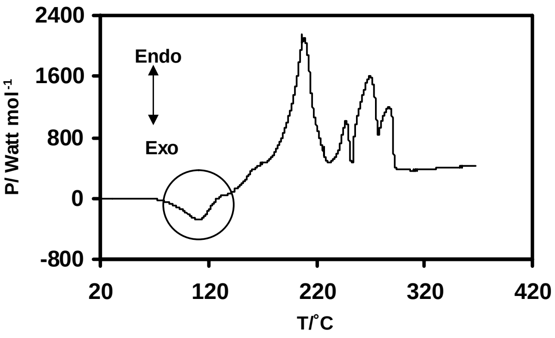


Fig. 1. DSC curve of $[Co(NH_3)_5(ONO)]Cl_2$ in a wide temperature range, linkage isomerization peak shown in circle.

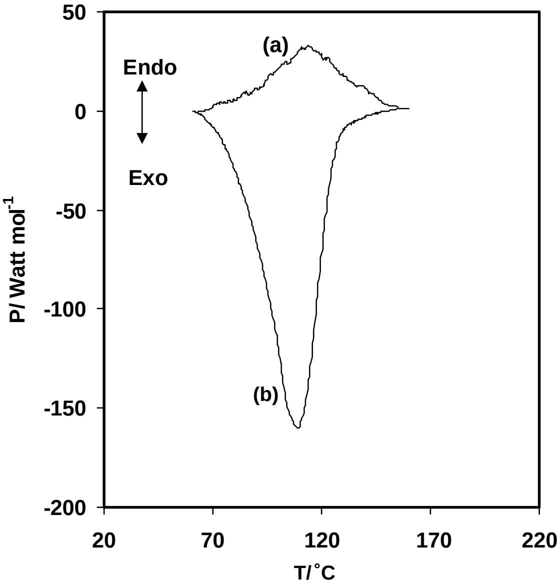
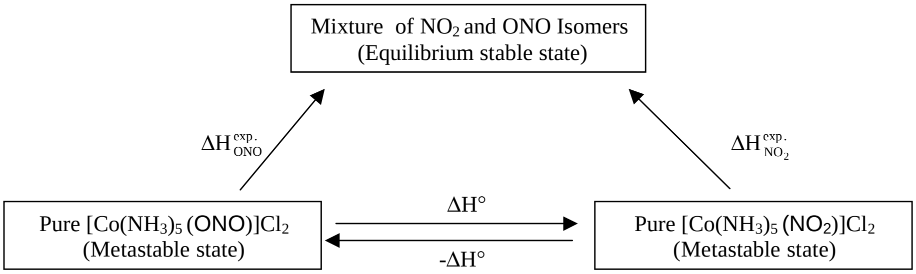


Fig. 2. DSC curves of isomerization of pure $[Co(NH_3)_5(NO_2)]Cl_2$ (a) and pure $[Co(NH_3)_5$ $(ONO)]Cl_2$ (b) in solid state.



Scheme 1. Enthalpy relationship of two metastable states, pure $[Co(NH_3)_5(ONO)]Cl_2$ and $[Co(NH_3)_5(NO_2)]Cl_2$, with equilibrium stable state in solid state.

of a hypothetical process in which total conversion of one isomer to another one occurs and could be determined by Eq. (2).

$$|\Delta H^{\text{hypo.}}| = |\Delta H^{\text{exp.}}_{NO_2}| + |\Delta H^{\text{exp.}}_{ONO}| \tag{2}$$

The negative value of $|\Delta H^{\text{hypo.}}|$ is equal to $\Delta H°$, total enthalpy change of conversion of nitrito to nitro isomer. If there is a linear relationship between amounts of evolved or adsorbed heat with extent of conversion, mole fractions of two isomers in the course of reaction can be obtained using Eq. (3).

$$\alpha_{NO_2}(T) = \frac{|\Delta H^{\text{exp.}}_{ONO}|}{|\Delta H^{\text{hypo.}}|} \qquad \alpha_{ONO}(T) = 1 - \alpha_{NO_2}(T) \tag{3}$$

As the conversion reaches to equilibrium state, the equilibrium constant simply could be written as:

$$K = \frac{\alpha_{NO_2}}{\alpha_{ONO}} \tag{4}$$

Using this K value, we can obtain $\Delta G°$ by Gibbs free energy equations:

$$\Delta G° = -RT \ln K, \qquad \Delta G° = \Delta H° - T\,\Delta S° \tag{5}$$

Knowing $\Delta G°$ and $\Delta H° (= \Delta H^{\text{hypo.}})$ from (2), we can get $\Delta S°$. The values of $\Delta G°$ and K at any temperature can be calculated using the $\Delta S°$ and $\Delta H°$.

The results of this investigation are given in Table 1. These data clearly show that the linkage isomerization of pure nitrito is mainly enthalpy driven, while nitro isomerization (reverse reaction) occurs due to slight increase in entropy.

The enthalpy value also allow us to compare the metal–ligand bond strength difference in two isomers and to conclude that N-bonded nitro Ligand makes a somewhat stronger bonding with cobalt(III) than O-bonded nitrito ligand. However, this bond strength difference is not so great that conversion of nitrito to nitro to be completely irreversible. The small enthalpy difference together with entropy factor favors the establishment of partially reversible reaction (1).

Table 1
Thermodynamic parameters of thermal reaction $[Co(NH_3)_5(ONO)]Cl_2 \Leftrightarrow [Co(NH_3)_5(NO_2)]Cl_2$ in solid state

$\Delta H^{\text{exp.}}_{ONO}$ (kJ mol^{-1})	−4.67 (±0.19)
$\Delta H^{\text{exp.}}_{NO_2}$ (kJ mol^{-1})	0.99 (±0.05)
$\Delta H°$ (kJ mol^{-1})	−5.66 (±0.20)
$\Delta S°$ (J K^{-1} mol^{-1}), 333 K	−0.36 (±0.80)
$\Delta G°$ (kJ mol^{-1}), 333 K	−5.54 (±0.20)
K, 333 K	7.72 (±0.8)

The cooling curve of the equilibrium stable state, achieved either by heating of pure nitrito or nitro samples, is not accompanied by detectable heat flow (Fig. 3). This is a evidence implying that nitro/nitrito interconversion is not a usual phase transition process in which one compound converts to another one upon changing temperature and vice versa, rather it occurs homogeneously in solid state which is hindered by kinetic barrier at ambient temperature. After establishment of the equilibrium, the relative amounts of two isomers are governed by Gibbs free energy relationship. This result also reveals that variation of heat content of the equilibrium state with changing temperature is not so great as to be observable by means of DSC.

3.2. Thermokinetic

Kinetic analysis of non-isothermal DSC curves of nitro/nitrito interconversion was performed by means of general differential method [19]. If there is two opposing reactions (Eq. (1)), the progress of nitrito isomerization can be represented by following relationship:

$$\frac{d\alpha_{NO_2}}{dT} = \left(\frac{1}{b}\right)[k_{ONO} f(\alpha_{ONO}) - k_{NO_2} f'(\alpha_{NO_2})] \tag{6}$$

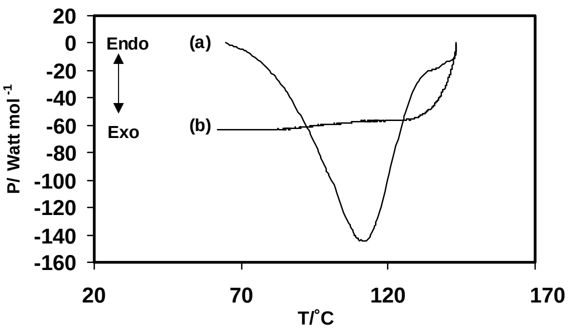


Fig. 3. (a) Heating DSC curve of pure $[Co(NH_3)_5(ONO)]Cl_2$. (b) Cooling curve of heated sample.

Table 2
Activation parameters of thermal isomerization reaction $[Co(NH_3)_5(ONO)]Cl_2 \Leftrightarrow [Co(NH_3)_5(NO_2)]Cl_2$

$\Delta H^{\ddagger}_{ONO}$ (kJ mol^{-1})	$\Delta S^{\ddagger}_{ONO}$ (J K^{-1} mol^{-1})	$\Delta H^{\ddagger}_{NO_2}$ (kJ mol^{-1})	$\Delta S^{\ddagger}_{NO_2}$ (J K^{-1} mol^{-1})	T (K)	State	Method	Reference
103 (±3)	−6 (±1)	108 (±5)	−3 (±2)	333	Pure solid	DSC	This Work
106	3	115	26	333	KBr pellet	IR	[2]
108	13	–	–	298	KBr pellet	IR	[4][a]
85	−64	95	−44	333	KBr pellet	IR	[18]
91.6 (±0.8)	−17 (±3)	–	–	298	Aqueous solution	UV-Vis	[5][a]
95 (±4)	+4 (±12)	–	–	298	Aqueous solution	UV-Vis	[6][a]
78 (±2)	29 (±3)	–	–	298	Liquid ammonia	UV-Vis	[7][a]
98 (±13)	+3 (±40)	–	–	298	PVA[b] matrix	UV-Vis	[15][a]
72	−78	72	−88	333	Aqueous solution	UV-Vis	[18]

[a] Assumed to be irreversible.
[b] Poly(vinyl alcohol).

where k_{ONO} and k_{NO_2} represent rate constants of forward and reverse reaction (1), respectively, f and f' are conversion functions of α dependent on the mechanism of reaction, and b is the linear heating rate, dT/dt.

Since isomerization reaction occurs homogeneously and intramolecularly in solid state [12,13], we may assume first order kinetic law for both forward and reverse directions, i.e. $f(\alpha_{ONO}) = \alpha_{ONO}$ and $f'(\alpha_{NO_2}) = \alpha_{NO_2}$. At initial stages of nitrito isomerization, we can neglect reverse term due to low mole fraction of nitro isomer and then Eq. (6) is simplified to:

$$\frac{d\alpha_{NO_2}}{dT} = \left(\frac{1}{b}\right)[k_{ONO}(T)\alpha_{ONO}] \tag{7}$$

The value of $k_{ONO}(T)$ is generally assumed to be governed by the Arrhenius equation:

$$k_{ONO}(T) = A_{ONO}\,e^{-E_{ONO}/RT} \tag{8}$$

where A_{ONO} and E_{ONO} are the pre-exponential factor and activation energy parameters of nitrio isomerization, respectively, and R is the gas constant.

Combing Eqs. (7) and (8) we obtain:

$$\ln\left[\frac{d\alpha_{NO_2}/dT}{\alpha_{ONO}}b\right] = \ln[k_{ONO}(T)] = \ln A_{ONO} - \frac{E_{ONO}}{RT} \tag{9}$$

Fig. 4 shows a representative kinetic plot of nitrito isomerization based on the kinetic Eq. (9). The linearity of the plot at initial stages of nitrito isomerization confirm the validity of the proposed model and the assumptions. Deviations of the curve from Eq. (9) at higher temperature are related to the decreasing the validity of the proposed initial rate method at high temperature, where the amount of nitro isomer would be significant and reverse isomerization could not be neglected. The Arrhenius parameters, A_{ONO} and E_{ONO} could be obtained from linear part of the curve as extrapolated intercept and slope, respectively. The activation enthalpy and entropy of the reaction could be calculated from the Arrhenius parameters as follows:

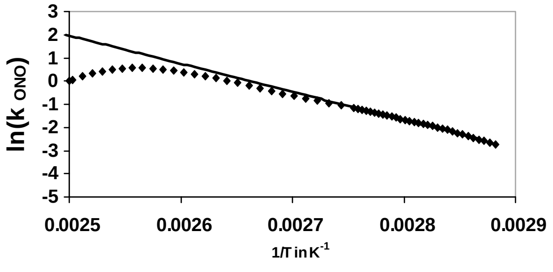


Fig. 4. Plot of $\ln(k_{ONO})$ vs. $1/T$ for isomerization reaction of $[Co(NH_3)_5(ONO)]Cl_2$.

$$\begin{aligned} \Delta H^{\ddagger}_{ONO} &= E_{ONO} \\ \Delta S^{\ddagger}_{ONO} &= R\ln\left[\frac{A_{ONO}}{kT/h}\right] \end{aligned} \tag{10}$$

The activation functions of reverse direction of equilibrium (1) could be similarly obtained, starting with pure nitro isomer. These results together with some previously reported data, obtained with spectral methods, are summarized in Table 2. The activation entropy and enthalpy values obtained here are consistent with intramolecular rearrangement mechanism suggested for the solution and solid state isomerization [4,13,15,16], in which transition state has higher coordination number and lower entropy with respect to reactants.

Most pervious solid state kinetic data of isomerization were obtained using IR spectroscopy [4,17,19], in which solid samples were highly pressurized through sample preparation step. In view of the fact that isomerization reaction is affected by complex's matrix in solid state [13], the values presented here, which are obtained for pure compounds, may be more realistic than IR data.

4. Conclusion

DSC was satisfactory employed for determination of thermodynamic and kinetic parameters of linkage isomerization reaction $[Co(NH_3)_5(ONO)]Cl_2 \Leftrightarrow [Co(NH_3)_5(NO_2)]Cl_2$ in solid state. In agreement with some pervious reports [2,18] and in contrast with some other ones [4–7,15], the results of present study showed that interconversion of both isomers should be considered as equilibrium reaction. Both pure isomers could be regarded as metastable states which convert to the same stable state, involving a mixture of both isomers, upon heating. The thermodynamic data revealed that stable state is closer to metastable state of pure nitro than that of pure nitrito, implying that contribution of N-bonded nitro isomer in stable state is more than O-bonded nitrito form. Isomerization of pure nitrito is enthalpy driven, while reverse isomerization of nitro isomer is slightly entropy driven.

Kinetic results showed that we may reliably assign a first order rate law to both forward and reverse directions. In accordance with previous reports, negative entropy of activation for both directions could be considered as an evidence of an intramolecular mechanism, involving formation of a seven coordinate transition state.

Both kinetic and thermodynamic results could be obtained by a few runs of DSC experiments within a limited time period, this is a distinguished advantageous of DSC over spectral methods.

Acknowledgements

The financial support of this work by research council of University of Mazandaran is gratefully acknowledged.

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