Scientia Iranica, Vol. 4, Nos. 1&2, pp 46–52
© Sharif University of Technology, July 1997

SCIENTIA
IRANICA

Solid State Kinetic Parameters and Mechanism for Deamination-Anation of Trans-$[Co^{III}(acacen)(amine)_2]$.NCS

M. Amirnasr*, R. Vafazadeh[1] and S. Alavi-Shoushtari[1]

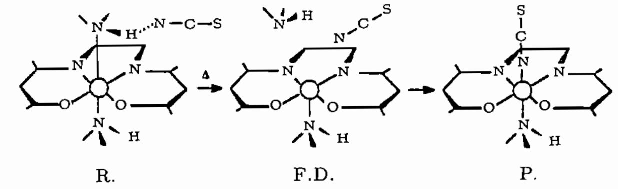
The solid state kinetic parameters for deamination-anation of trans-$[Co(acacen)(amine)_2]$.NCS (with amine = piperidine (pprdn), 1, benzylamine (bzlan), 2, morpholine (mrpln), 3, pyrrolidine (prldn), 4, and acacen = N,N′-ethylenebis(acetylacetoneiminato) dianion) have been studied by thermogravimetric measurements under both isothermal and nonisothermal conditions, and infrared and visible spectroscopy. Heating at controlled temperature and time, indicated that compounds 1, 3 and 4 produce trans-[Co(acacen)(amine)(NCS)], whereas compound 2 gives trans-[Co(acacen)(amine)(SCN)]. The values of the activation energy and the activation entropy were 112.5 ± 15.9 kJ mol^{-1} and -49.8 ± 4.9 J K^{-1} mol^{-1} for 1; 126.5 ± 2.3 kJ mol^{-1} and -512.1 ± 6.7 J K^{-1} mol^{-1} for 2; 98.0 ± 8.3 kJ mol^{-1} and -102.0 ± 2.5 J K^{-1} mol^{-1} for 3; and 132.0 ± 19.7 kJ mol^{-1} and -15.1 ± 5.9 J K^{-1} mol^{-1} for 4. A dissociative mechanism is proposed with an activated complex of square-based-pyramidal geometry.

INTRODUCTION

Solid-state reactions of coordination compounds have been studied for many years [1-7]. The deamination-anation reactions of the type:

$$[M(A\text{-}A)_3]X_3(s) \xrightarrow{\Delta} [M(A\text{-}A)_2X_2]X(s) + (A\text{-}A)(g),$$

have been investigated, where M = Cr(III), Co(III), Fe(II) or Ni(II); X = Cl, Br, I, NCS, etc. and (A-A) = bidentate groups [1,8]. Studies have also been conducted using hexaammine complexes, and Ohyoshi et al. [9] have studied the deamination of $[Cr(NH_3)_6]X_3$ (where X is Cl or Br) in the solid state using thermal methods. In a recent review, House [10] has provided an elegant outline of the many factors which must be taken into account when considering the kinetic data and the mechanisms for anation reactions in the solids. It is generally accepted that the deamination-anation reaction can, in most cases, be interpreted in terms of formation of a nonionic Frenkel defect. That is, the reaction begins with the loss of an amine molecule and proceeds by the diffusion of the Frenkel defect through the lattice (Scheme 1). Although the intimate mechanism may be dissociative, there will be some differences in the kinetic parameters and the form of the rate laws depending on the nature of the coordinated amines.



Scheme 1. Formation of a nonionic Frenkel defect in a deamination-anation process.

In this paper, the results obtained by isothermal and nonisothermal measurements on the complexes trans-$[Co(acacen)(amine)_2]$.NCS, 1–4, are given and the influence of the amine ligand on the magnitude of the kinetic parameters are explained.

EXPERIMENTAL SECTION

The complexes trans-$[Co(acacen)(amine)_2]$.NCS, 1–4, were prepared by the methods described elsewhere [11]. Infrared spectra were recorded on a Shimadzu 435 IR spectrophotometer. Samples were prepared by using the KBr technique. Electronic absorption spectra were recorded in solution on a Shimadzu UV-240 spectrophotometer. Thermogravimetric measurements

---

*. *Corresponding author, Department of Chemistry, Isfahan University of Technology, Isfahan, 84156, I.R. Iran.*

[1] *Department of Chemistry, Isfahan University of Technology, Isfahan, 84156, I.R. Iran.*

were performed using Polymer Laboratories Model STA 625 and Polymer Laboratories Model TGA 1500 instruments under nitrogen gas (10 cm^3 min^{-1}), the sample size being in the range of 4-7 mg. The heating rate for nonisothermal experiments was 2°C/min. To resolve the nonisothermal TG curves, the widely employed approximation of Coats and Redfern [12] was used.

From nonisothermal TG curves, several temperatures were selected in the anation interval to carry out the isothermal TG runs necessary to calculate the kinetic parameters. Under isothermal conditions, the Arrhenius method was used.

RESULTS AND DISCUSSION

Typical TG and DSC curves for trans-[Co(acacen)(amine)$_2$].NCS, 1–4, are shown in Figure 1. These complexes endothermically lose one of the amine ligands (the H-bonded one) to produce trans-amineisothiocyanato complex from 1, 3 and 4 and trans-aminethiocyanato from 2. The thermal decomposition reaction can be expressed by Equation 1:

$$\text{trans-[Co(acacen)(amine)}_2\text{].NCS} \xrightarrow{\Delta}$$

$$\text{trans-[Co(acacen)(amine)(NCS)]} + \text{amine}, \qquad (1)$$

where amine = pprdn, bzlan, mrpln, prdln.

The cobalt complexes produced from Equation 1 were also synthesized directly as reported elsewhere [11]. The thermal decomposition products were thus identified from the results of UV-Vis and IR spectral measurements and a comparison with the spectroscopic properties of those produced by direct synthesis (Table 1a). The product of compound 2 was identified as the S-bonded thiocyanato complex from the results of UV-Vis and IR spectral measurements.

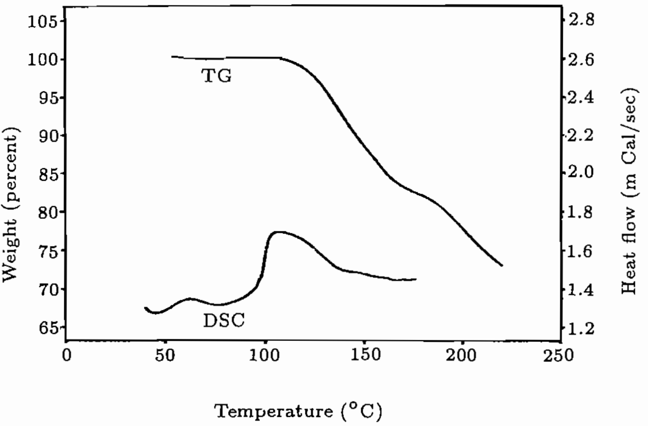


Figure 1. Typical TG and DSC curves for trans-[Co(acacen)(amine)$_2$].NCS (amine = pprdn). The reaction is endothermic.

Table 1a. Spectral data for complexes 1–4 and their thermal products [11].

Complex*	λ_{max}(nm) LF$_1$	ν_{CN}(NCS) (cm^{-1})
1. [A(pprdn)$_2$].NCS	437	2052
[A(pprdn)(NCS)]^d	442	2122
[A(pprdn)(NCS)]^t	442	2122
2. [A(bzlan)$_2$].NCS	406	2061
[A(bzlan)(NCS)]^d	430	2120
[A(bzlan)(SCN)]^t	445	2138
3. [A(mrpln)$_2$].NCS	444	2065
[A(mrpln)(NCS)]^d	449	2122
[A(mrpln)(NCS)]^t	449	2122
4. [A(prldn)$_2$].NCS	417	2065
[A(prldn)(NCS)]^d	438	2122
[A(prldn)(NCS)]^t	438	2122

*A = Co(acacen), d = by direct synthesis,
t = by thermal anation.

The single sharp band due to ν(CN) of the NCS anion [13] (hydrogen bonded to the coordinated amines [11]) which appears at 2052, 2061, 2065, and 2065 cm^{-1} in the IR spectra of the parent complexes 1, 2, 3 and 4 respectively, disappears upon heating (Figure 2). However a new sharp band appears at about 2120 cm^{-1} in the IR spectra of the thermal products resulted from 1, 3 and 4 and at 2138 cm^{-1} for that resulted from complex 2. The new band is indicative of a coordinated NCS group which, in the case of 1, 3 and 4, appears to be N-bonded while it is S-bonded in the thermal product of complex 2. The stretching frequency of a bridging NCS ligand also increases to 2135-2180 cm^{-1} [14]. Therefore, a bridged complex may also be speculated as the thermal product of complex 2. However, a comparison between the results of this experiment and the reported data on the infrared and electronic spectra (vide infra) of some related cobalt complexes [14,15] gives no support to this alternative. The ν(CN) of the bridging NCS appears at 2170, 2175, 2180 cm^{-1} for [(NH$_3$)$_5$CoSCNCo(CN)$_5$], [(NH$_3$)$_5$CoNCSCo(CN)$_5$] and K$_4$[(CN)$_5$Co(NCS)$_2$ Co(CN)$_4$] complexes respectively [14]. Most importantly, a bridged species would necessitate the presence of ν(CN) band of free SCN$^-$ in the infrared spectrum due to the stoichiometry of the system [15]. Characteristic changes are also observed in the (N-H) stretching regions (Figure 2). Since only one ν(N-H) is observed in the N-H stretching region of the coordinated amine in the thermal products of 1, 3 and 4 (3145, 3175 and 3180 cm^{-1} respectively), the hydrogen bonded amine is presumably replaced by NCS group. The N-H stretching region of the thermal product of 2 is somehow different from that of trans-[Co(acacen)(bzlan)(NCS)] with an

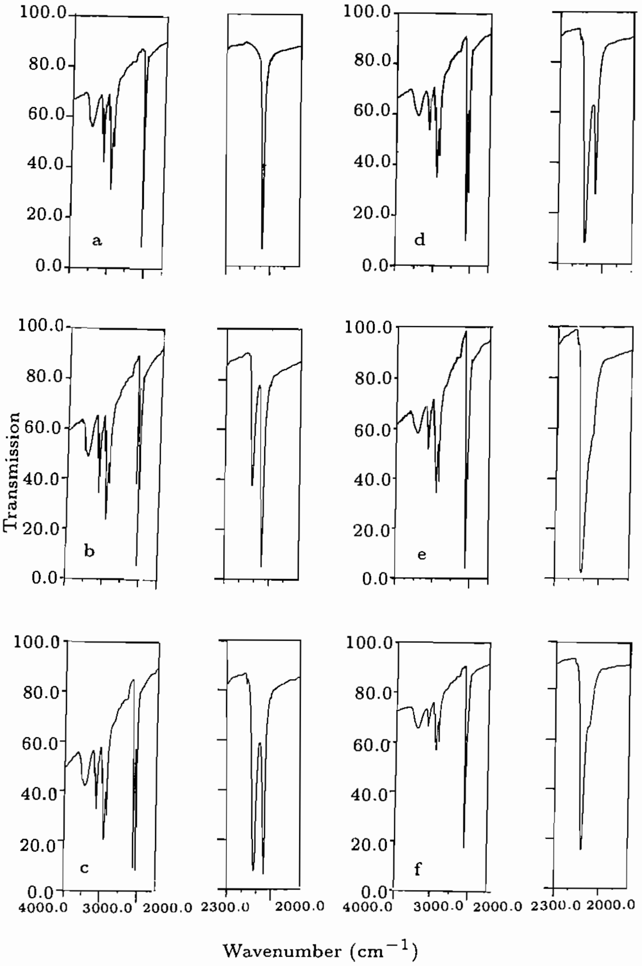


Figure 2. Infrared spectra of complex 1. a: before heating; b: after 1h; c: after 2h; d: after 4h; e: after prolonged heating; (at 110°C) f: thermal product by direct synthesis. The 2300-2000 cm^{-1} region has been expanded. The spectra of other complexes show similar changes (see Table 1a).

N-bonded NCS group, which has been prepared by direct synthesis [11]. This would be expected, because the S-bonded thiocyanato would not participate in intermolecular hydrogen bonding as the N-bonded isomer does. Therefore, a less complex N-H stretching region is observed for the S-bonded thermal product.

The electronic spectra of the thermal products show a longer $\lambda_{max}(LF_1)$ relative to that for the parent complexes. The observed shift, which is due to replacing one of the axial amines by a weaker NCS ligand, is more noticeable for prldn (21 nm) and bzlan (39 nm) than for mrpln (5 nm) and pprdn (5 nm) (Table 1a). The relatively high shift for complex 2 is due to the formation of the S-bonded complex which is in agreement with similar cases reported in the literature [14,16]. There is a red shift of about 15 nm in the λ_{max} of the first ligand field absorption band on going from the N-bonded to the S-bonded thiocyanate in a series of Co(III) complexes (Table 1b). The first ligand field band for trans-[Co(acacen)(bzlan)(NCS)], produced by direct synthesis, appears at 430 nm, whereas that for the deamination-anation product of complex 2 appears at 445 nm. The observed difference of 15 nm in the λ_{max} of the first ligand field band, along with the infrared spectral data, indicates that the S-bonded structure is the most probable for the thermal product of complex 2.

Table 1b. $\lambda_{max}(LF_1)$ for the linkage isomers of thiocyanatocobalt(III) complexes.

Complex	λ_{max} (nm)	$\Delta\lambda$ (nm)	Ref.
$[(CN)_5Co\text{-}SCN]^{3-}$	378		[14]
$[(CN)_5Co\text{-}NCS]^{3-}$	363	15	[14]
$[(NH_3)_5Co\text{-}SCN]^{2+}$	512		[14]
$[(NH_3)_5Co\text{-}NCS]^{2+}$	497	15	[14]
trans-[(acac)$_2$(py)Co-SCN]	571		[15]
trans-[(acac)$_2$(py)Co-NCS]	558	13	[15]
trans-[(acacen)(bzlan)Co-SCN]	445		p.w.*
trans-[(acacen)(bzlan)Co-NCS]	430	15	p.w.*

* p.w. = present work

KINETICS

The Coats-Redfern [12] method was applied to the data obtained from the deamination anation reactions. Analysis by Coats-Redfern method involving the function g(α) which depends on the processes controlling the solid state reaction rates, gave the best fit using computer simulations.

Kinetic parameters are very difficult to calculate only by nonisothermal TG curves [17-19] due to ignorance of the true g(α) expressions. It is necessary to compare the results obtained by nonisothermal and isothermal TG measurements for all the g(α) expressions in order to calculate the true activation energy and to infer the physical mechanism for the solid state process. Therefore, not only the nonisothermal TG curves (Figure 1), but also the isothermal TG curves at three different temperatures (Figure 3) for each compound have been recorded. Using the isothermal data, the best fitting function of a group of Avrami Erofeyev functions (Table 2) was found. Figure 4 shows the degree of fitting for the best function. It is expected to obtain a straight line for the best function. Based on the results obtained from curve fitting, the functions F_1 and $A_{3/2}$ give the best fit for deamination-anation reaction of 1, 3 and 4 complexes and that of complex 2 respectively.

A typical first order rate plot for the deamination-anation reaction of 1, 3 and 4 complexes which fit the first-order equation:

$$-\ln(1-\alpha) = kt$$

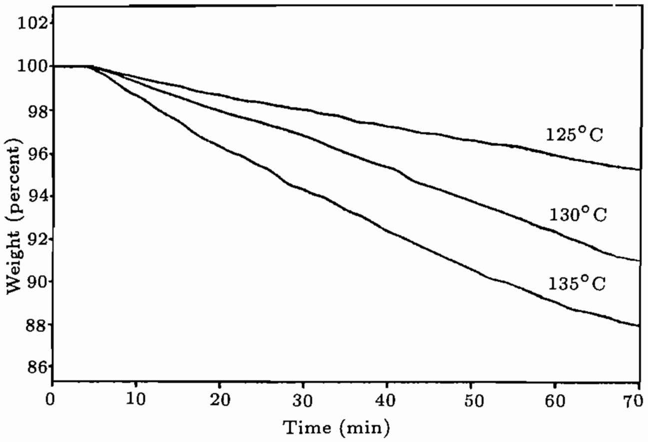


Figure 3. Isothermal TG curves (indicating the temperature) for trans-[Co(acacen)(prldn)$_2$].NCS 1 (compounds 2, 3 and 4 show very similar curves).

Table 2. Selected functions used for kinetic studies.

Function	
Notation	**g(α)**
F_1	$-\ln(1-\alpha)$
$A_{3/2}$	$[-\ln(1-\alpha)]^{2/3}$
A_2	$[-\ln(1-\alpha)]^{1/2}$
A_3	$[-\ln(1-\alpha)]^{1/3}$
A_4	$[-\ln(1-\alpha)]^{1/4}$
R_1	α
R_2	$1-(1-\alpha)^{1/2}$
R_3	$1-(1-\alpha)^{1/3}$
D_1	α^2
D_2	$(1-\alpha)\ln(1-\alpha)+\alpha$
D_3	$[1-(1-\alpha)^{1/3}]^2$
D_4	$(1-2\alpha/3)-(1-\alpha)^{2/3}$

is shown in Figure 5a, and the rate plot for complex 2 which fits the $A_{3/2}$ rate equation,

$$[-\ln(1-\alpha)]^{2/3}=\mathrm{kt},$$

is shown in Figure 5b. The temperature dependence of the rate constants conform to the Arrhenius rate law (Figure 6). The rate parameters of 1, 3 and 4 were also determined from their corresponding nonisothermal curves using the expression:

$$\ln[-\ln(1-\alpha)/\mathrm{T}^2]=\ln[(\mathrm{AR}/\mathrm{E_a})(1-2\mathrm{RT}/\mathrm{E_a})] - \mathrm{E_a}/\mathrm{RT},$$

and the following relation (with n = 3/2) for complex 2,

$$\ln\{[1-(1-\alpha)^{1-\mathrm{n}}]/\mathrm{T}^2(1-\mathrm{n})\} = \ln[(\mathrm{AR}/\mathrm{E_a})(1-2\mathrm{RT}/\mathrm{E_a})]-\mathrm{E_a}/\mathrm{RT},$$

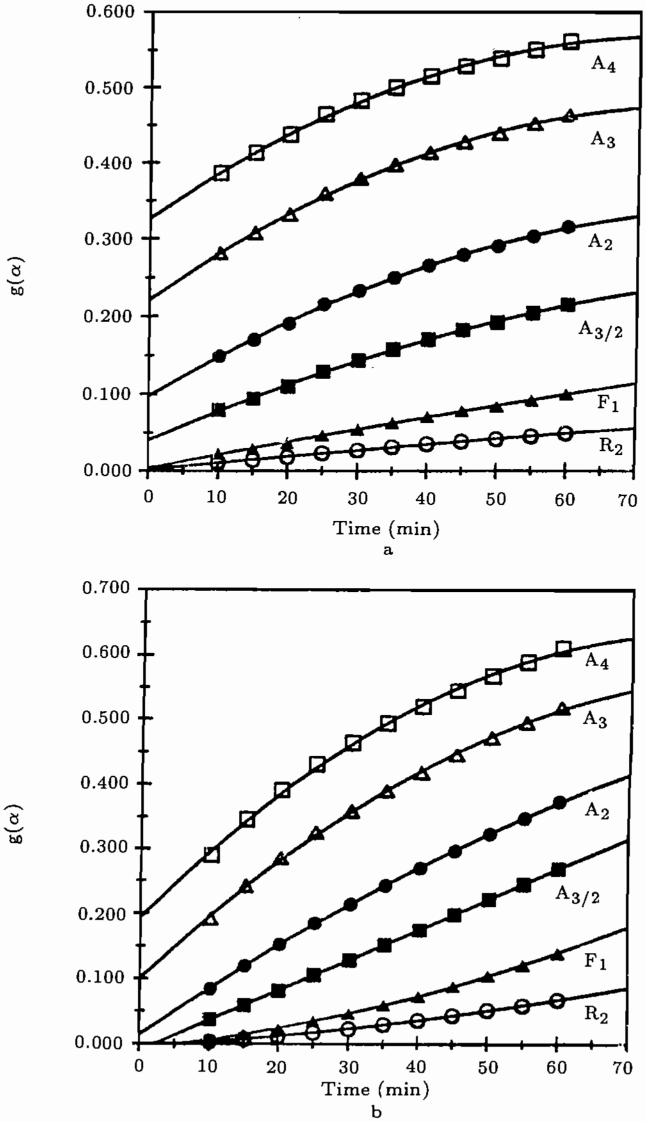


Figure 4. Kinetic analysis for: a) pprdn complex at 110°C, b) bzlan complex at 135°C, under isothermal conditions.

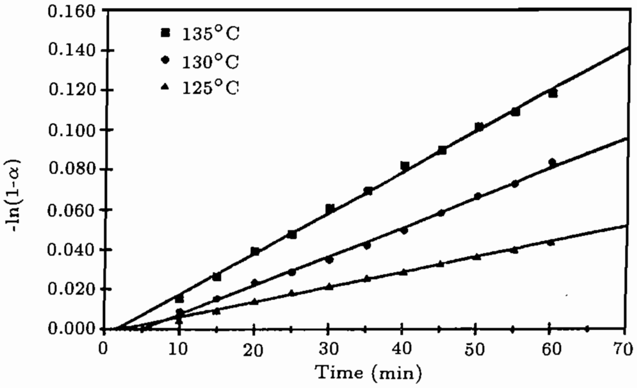


Figure 5a. Plots of first-order rate equation (F_1) for deamination-anation reaction of prldn complex 1.

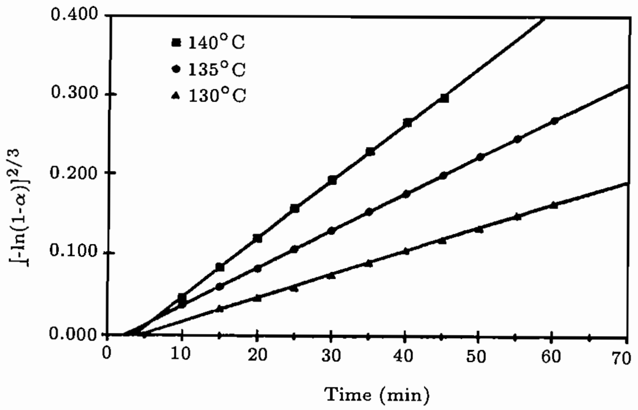


Figure 5b. Plots of the rate equation ($A_{3/2}$) for deamination-anation of bzlan complex 2.

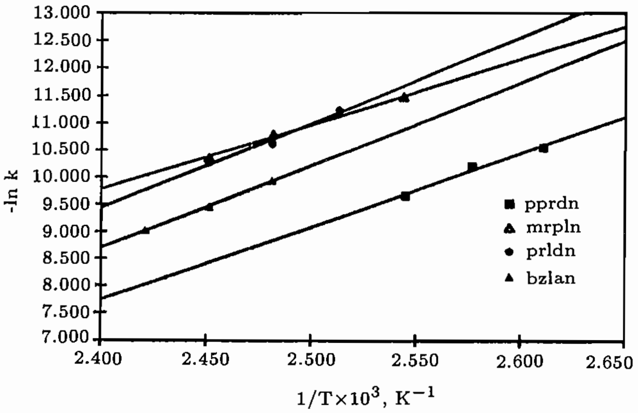


Figure 6. Arrhenius plots of deamination-anation reactions for pprdn 1, bzlan 2, mrpln 3 and prldn 4 compounds.

derived by Coats and Redfern [12]. The kinetic parameters for complexes 1-4 obtained by the linear heating method agree well with those from isothermal measurements (Table 3). The activation enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) were calculated by the following equation:

$$\Delta H^{\neq} = E_a - RT \quad \text{and}$$

$$\Delta S^{\neq} = R[\ln(Ah/\kappa k_B T) - 1],$$

where κ is the transmission constant ($\kappa = 1$) and R, A, h, k_B and T, have their usual meanings.

From the results of Table 3, two points are found for discussion: (a) E_a is low, in all the cases; (b) E_a varies with the amine ligands.

With regard to (a) and according to the mechanisms proposed by House [20] for the thermal anation reactions of solid complexes, high values of E_a have a better correspondence with an S_N2 mechanism (forming a Schottky-type defect) while low values have a better correspondence with S_N1 (forming a Frenkel-type defect). In this case, in spite of the proximity of NCS to the metal center, an S_N2 mechanism is unlikely for the anation reaction. In an S_N2 process the formation of a seven-coordinated complex (pentagonal bipyramidal) based on a crystal field model requires 8.25 Dq [21] (Dq being in the range of 27.0 - 29.5 kJ mol^{-1} for complexes 1–4 [11]), that is about 230 - 251 kJ mol^{-1} greater than the E_a found. The energy required for the formation of an activated complex with an octahedral wedge geometry is only 3.63 Dq (about 98 - 107 kJ mol^{-1}, being close to the E_a found).

Table 3. Rate constants and kinetic parameters of the deamination-anation reactions for complexes 1-4.

Complex (amine)	**Function**	**k × 10^5 s^{-1} (Temp., °C)**	**$E_a \pm \sigma$ (kJ mol^{-1})**	**$\Delta H^{\neq} \pm \sigma$ (kJ mol^{-1})**	**$\Delta S^{\neq} \pm \sigma$ (J K^{-1}mol^{-1})**	**A s^{-1}**
(1) (pprdn)	F_1	2.61 (110) ±0.03 3.71 (115) 6.39 (120)	112.5 ±15.9	109.3 ±15.9	-49.8 ±4.9	5.50 × 10^{10}
(2) (bzlan)	$A_{3/2}$	4.85 (130) ± 0.04 7.77 (135) 12.09 (140)	126.5 ± 2.3	123.1 ± 2.3	-512.1 ± 6.7	1.22 × 10^{12}
(3) (mrpln)	F_1	1.03 (120) ±0.02 2.04 (130) 3.18 (135)	98.0 ± 8.3	94.6 ± 8.3	-102.0 ±2.5	1.07 × 10^8
(4) (prldn)	F_1	1.31 (125) ± 0.03 2.45 (130) 3.44 (135)	132.2 ± 19.7	128.8 ± 19.7	-15.1 ± 5.9	3.70 × 10^{12}

However, considering that in the S_N2 reaction the formation of a Schottky defect, by moving the anion from its lattice position, is known to involve a high energy ($E_{\text{deffect}} = 0.24\ U, U =$ lattice energy) [22], the observed activation energies are too low for an S_N2 process.

The intimate mechanism may, therefore, be dissociative with the formation of a square-base-pyramid activated complex, requiring only 4.00 Dq [21] (activation energy in the range of 108–118 kJ mol^{-1}). The transition state is, thus, determined by amine loss and a nonionic Frenkel defect formation (Scheme 1).

With respect to (b), the variation of the activation energy is expected to be parallel to the metal-amine bond strength if an S_N1 mechanism is operative, and the rate of deamination depends upon the rate at which metal-ligand bonds are broken. This is in accord with the experimental results. The observed sequence: prldn > pprdn > mrpln for the values of E_a (Table 3) is similar to that for the Dq values of these complexes. The observed E_a value for bzlan complex 2, which does not fit the expected order, may have an origin in the size of bzlan, which is quite different from that of the other three amines. This is supported by the highest negative value of $\Delta S^{\neq}$ for complex 2.

The entropy effect may be explained by the relative sizes of the anions and cations and free space between the ions. A large free space will make it easier for the released amine molecule to slip into an interstitial position, causing little or no lattice distortion. Therefore, the entropy of activation may be small or slightly negative. Effectively, the radius of the NCS^- (1.99Å [23]) is quite different from the radius of the voluminous cation (about 8Å [11]) resulting in a large free volume. Considering the role of the free space, the observed negative values of $\Delta S^{\neq}$ may then be rationalized. With respect to the highest value of $\Delta S^{\neq}$ (-512.1 J K^{-1} mol^{-1}) for complex 2, the following possibility may be pointed out: If a dissociative mechanism is assumed, in which the transition state is determined by Co-N(amine) bond rupture, detachment of the amine with a longer chain is expected to be accompanied by a more negative $\Delta V^{\neq}$ and $\Delta S^{\neq}$ in the activation process. This is because an amine with a longer chain provides more free space and it is also more likely for such an amine to fold and attain a more compact structure. For example, the $\Delta S^{\neq}$ of deaquation-anation, which is accompanied by isomerization, is reported to be −28.24 and −178.61 J K^{-1} mol^{-1} for trans-$[CrF(en)_2(H_2O)]Br_2$ and trans-$[CrF(tn)_2(H_2O)]Br_2$ respectively (en = ethylenediamine and tn = 1, 3-diaminopropane) [24].

The results obtained in the present work are consistent with a dissociative mechanism in which a nonionic Frenkel defect with a square-base-pyramid structure is formed. The Co-N(amine) bond rupture is the dominant process controlling the rate of deamination-anation reaction in these cobalt complexes and this is confirmed by the parallel trends observed in the activation energy and the strength of Co-N(amine) bonds.

CONCLUSION

The solid state deamination-anation reaction of trans-$[Co(acacen)(amine)_2].NCS$ complexes have been studied under both nonisothermal and isothermal conditions. There seems to be a good correlation between E_a values (ranging from 98.0 ± 8.3 to 132.2 ± 19.7 kJ mol^{-1}) and the values of 4 Dq (being in the range of 108–118 kJ $mole^{-1}$) for different amines. Thus, the transition state is determined by amine loss and a dissociative mechanism can be operative. The resulting pentacoordinated species, then, reacts with NCS^- to give the anation product. The mode of coordination of NCS, which is N-bonded for the anation products of 1, 3 and 4 and S-bonded for that of complex 2, is confirmed by IR and UV-Vis spectroscopy.

The negative values of activation entropy for the complexes 1–4 reflect the role of the free space between the ions. The highest value of $\Delta S^{\neq}$ observed for bzlan complex, 2, is also a consequence of a larger free space for this complex relative to 1, 3 and 4.

ACKNOWLEDGMENT

We gratefully acknowledge financial support from the I.U.T. Research Council. We wish to thank the Polymer Research Center of Iran for assistance with the thermogravimetric measurements. We also would like to thank Professor M. Ghiaci for helpful discussions.

REFERENCES

1. House, Jr., J.E. and Bailar Jr., J.C. "Mechanistic considerations for anation reactions in the solid state", *J. Am. Chem. Soc.*, **91**, pp 67–71 (1969), and references therein.
2. Nagase, K. and Yokobayashi, H. "Thermal deaquation-anation reactions of aquapentaamminechromium(III) complexes in the solid state", *Bull. Chem. Soc. of Japan*, **47**, pp 2036–2039 (1974).
3. Smith, J.P. and Wendlandt, W.W. "Mechanism of thermal deaquation of some transition metal aquoammine complexes", *Nature*, London, **201**, pp 291–292 (1964).
4. Wendlandt, W.W. and Bear, J.L. "The thermal deaquation of some aquopenta-amminecobalt(III) complexes", *J. Phys. Chem.*, **65**, pp 1516–1519 (1961).
5. Ribas, J. and Monfort, M. "Kinetic parameters and solid-state mechanism of the thermal dehydration of aquapentaammineiridium trihalide $[Ir(H_2O)(NH_3)_5]X_3(X = Cl^-, Br^-, I^-)$", *Thermochim. Acta*, **91**, pp 115–125 (1986).

6. Ribas, J. and Monfort, M. "Kinetic parameters and solid-state mechanism of the thermal dehydration of $[M(H_2O)(NH_3)_5][Co(CN)_6]$ [M = Co(III), Rh(III), and Ir(III)]", *Thermochim. Acta*, **76**, pp 201–211 (1984).

7. Ribas, J., Escuer, A. and Monfort, M. "Solid-state kinetic parameters and mechanism of the deaquation-anation of hexacyanochromate(III) and nitrosylpentacyanochromate(I) of aquo-pentaamminechromium(III), -cobalt(III), -rhodium(III) and -iridium(III)", *Inorg. Chem.*, **24**, pp 1874–1878 (1985).

8. Yamasaki, S., Fujiwara, T. and Yamamoto, Y. "Effect of lattice anions on the ligand substitution reaction of tris(1, 10-phenanthroline)metal(II) complexes: $[M(phen)_3]SO_4$ and $[M(phen)_3]X_2$ (M: Fe(II), Co(II), Ni(II); X: Cl^-, Br^-, I^-)", *Bull. Chem. Soc. of Japan*, **60**, pp 2565–2571 (1987).

9. Ohyoshi, A., Haraki, S., Odate, T., Kohata, S. and Oda, J. "Studies of ruthenium complexes. VIII. Kinetic studies of the thermal substitution reaction of hexaammine and cis-dihalogenotetraammineruthenium(III) Complexes in the solid state", *Bull. Chem. Soc. of Japan*, **48**, pp 230–233 (1975).

10. House Jr., J.E. "Mechanistic consideration for anations in the solid state", *Coord. Chem. Rev.*, **128**, pp 175–191 (1993).

11. Amirnasr, M. and Vafazadeh, R. "Synthesis and characterization of trans-$[Co^{III}(acacen)L_2]$.NCS, trans-$[Co^{III}(acacen)L_2]$G104 and trans-$[Co^{III}(acacen)(NCS)L]$ (L = piperidine, benzylamine, morpholine, pyrrolidine). X - ray structure determination of trans-$[Co(acacen)(pprdn)_2]$.NCS containing N-H ... NCS Hydrogen bond", *J. Scientia Iranica*, Sharif University of Technology, I.R. Iran, **4**(1&2) (1997).

12. Coats, A.W., Redfern, J.P. "Kinetic parameters from thermogravimetric data", *Nature*, London, **201**, pp 68–69 (1964).

13. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd. Edn., Wiley, New York, USA, p 272 (1978).

14. Wardeska, J.G. and Buckley, R.C. "The linkage isomerism of bridging thiocyanate in binuclear complexes", *Inorg. Chem.*, **11**, pp 1723–1726 (1972).

15. Boucher, L.J. and Herrington, D.R. "Stereochemistry of β-diketone complexes of cobalt(III). XIII. Linkage and geometrical isomers of thio-cyanatopyridinebis(acetylacetonato)cobalt(III)", *Inorg. Chem.*, **13**, pp 2290–2293 (1974).

16. Pearson, R.G. "Hard and soft acids and bases", *J. Am. Chem. Soc.*, **85**, pp 3533–3539 (1963).

17. Zsako, J. "Kinetic analysis of thermogravimetric data. VI. Problems of deriving kinetic parameters from TG [Thermogravimetric] curves", *J. Therm. Anal.*, **5**, pp 239–251 (1973).

18. Criado, J.M., Morales, J. and Rives, V. "Computer kinetic analysis of simultaneously obtained TG and DTG curves", *J. Therm. Anal.*, **14**, pp 221–228 (1978).

19. Bamford, D.H., Ed., *Compr. Chem. Kinet.*, **22**, Chapter 3 (1980).

20. House, J.E. "A proposed mechanism for the thermal reactions in solid complexes", *Thermochim. Acta*, **38**, pp 59–66 (1980).

21. Basolo, F. and Pearson, R.G. *Mechanism of Inorganic Reactions*, 2nd Edn., Wiley, New York, USA, Chapter 3 (1967).

22. Schmalzreid, H. *Solid State Reactions*, Verlag Chemie, New York, USA, p 23 (1974).

23. Huheey, J.E. *Inorganic Chemistry*, 3rd. Edn., Harper and Row, London, p 78 (1983).

24. Corbella, M. and Ribas, J. "Solid-state kinetic parameters and mechanism for the deamination-anation of trans-[Fluoroaquabis(diamine)chromium(III) complexes containing chloride, bromide, iodide and dithionate. Influence of amine size, entring anion, and trans to cis isomerization", *Inorg. Chem.*, **25**, pp 4390–4395 (1986).