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Thermal decomposition of *trans*-difluoro *bis*-(ethylenediamine) chromium (III) chloride 1.5 hydrate and μ-[(ethylenediamine) chromium (III) dichloro-(ethylenediamine)] chloride

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Abstract

Two complexes *trans*-difluoro *bis*-(ethylenediamine) chromium (III) chloride 1.5 hydrate and μ-[(ethylenediamine) chromium (III) dichloro (ethylenediamine)] chloride were isolated and were characterized by elemental analysis and IR spectroscopy. The thermal behaviour of the two complexes on heating up to 800°C in nitrogen atmosphere was examined by thermogravimetry (TG), DTG and differential thermal analysis (DTA). Thermal analysis showed three stages of decomposition of *trans*-$[Cr(en)_2F_2]Cl\cdot 1.5H_2O$ in the following order: (i) dehydration, (ii) deamination or loss of amine and (iii) total disruption of the complex to form Cr_2O_3. As for $[(Cr_2(en)_3Cl_4)]Cl_2$, its decomposition involved: (i) loss of the bridged ethylenediamine, (ii) loss of the two other ethylene diamines and (iii) disruption of the complex to form the oxide. Activation parameters were evaluated using the theory of absolute reaction rate and values of activation energy were found to be 38.3 and 103 kJ mol^{-1} for the dehydration and deamination of *trans*-$[Cr(en)_2F_2]Cl\cdot 1.5H_2O$ respectively, and 88.7 and 203 kJ mol^{-1} for the loss of bridged ethylene diamine and the other two ethylenediamines of $[Cr_2(en)_3Cl_4]Cl_2$ molecules, respectively. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thermal decomposition; *Trans*-difluoro *bis*-(ethylenediamine) chromium (III) chloride 1.5 hydrate; μ-*[(ethylenediamine) chromium (III) dichloro-(ethylenediamine)] chloride*

1. Introduction

Modern thermal analysis is largely based on advances in solid-state chemistry and it is believed that it would be useful to aquaint the experts in the area of thermal analysis with those problems of modern solid-state chemistry. One of these problems is the reactivity of solids. In classical chemistry, reactivity means the characteristics of the chemical activity of substances which involve, first, the variety of chemical reactions in which a given species takes part, and secondly, the rates of chemical reactions of these substances. The main factor determining reactivity is the composition and structure of molecules. As a measure of reactivity, the rate constant of a reaction is used, which can be measured from thermal analysis for solid-state reactions.

Thermal decomposition of solid complexes were extensively studied. Complexes of Cr(III) were the subject of earlier work by Bailar and co workers [1,2], Bear and Wendlandt [3], Corbella et al. [4], Bucci et al. [5], Narang et al. [6] and Revento et al. [7].

The present study deals with the thermal decomposition and effect of heating rates on the kinetic

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Table 1
Chemical analysis for complex (1) and (2)

	Cr^{3+}	C	N	Cl	H
Complex (1)					
Experimental value	19.14	17.68	20.41	12.8	6.6
Theoretical value	19.08	17.61	20.54	13.03	6.97
Complex (2)					
Experimental value	20.7	14.65	16.4	41.9	4.62
Theoretical value	20.93	14.49	16.9	42.86	4.83

parameters of the non-isothermal dehydration and decomposition of *trans*-difluoro *bis*-(ethylenediamine) chromium (III) chloride 1.5 hydrate and also the thermal decomposition of μ-[(ethylenediamine) chromium (III) dichloro ethylenediamine)] chloride.

2. Experimental

Chemicals: All chemicals were of pure grade (B.D.H. and Merck) and were used without further purification.

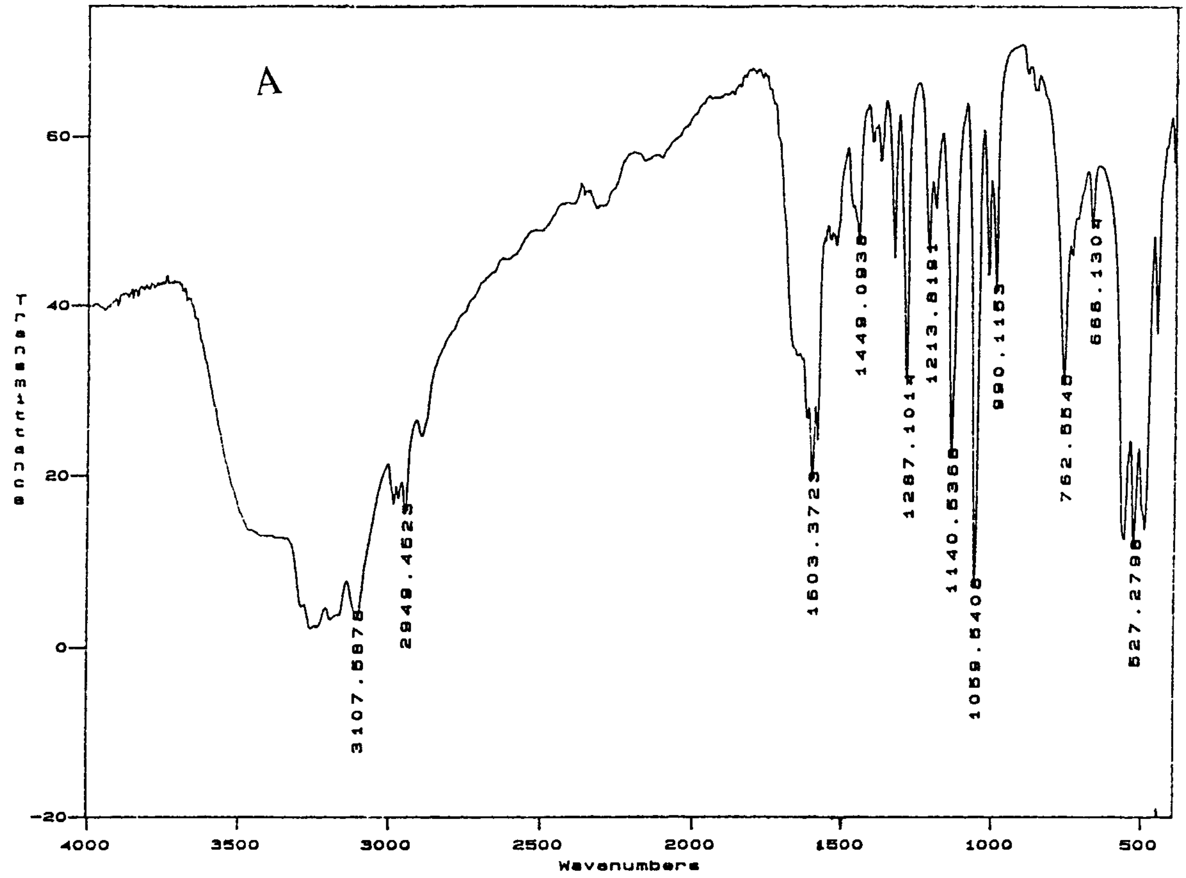

Fig. 1. IR spectra of (A) complex (1) and (B) complex (2).

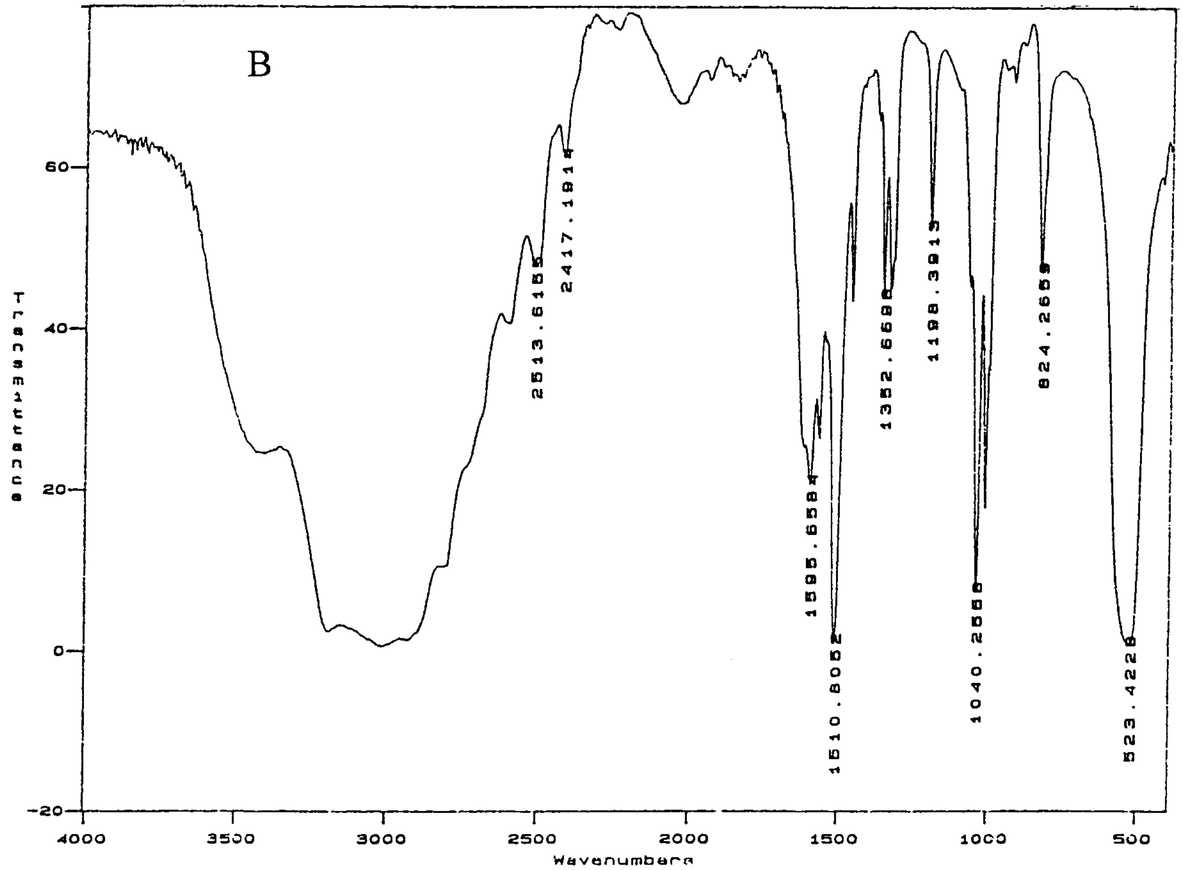

Fig. 1. (*Continued*).

2.1. Preparation of complexes

Trans-difluoro *bis*-(ethylenediamine) chromium (III) chloride 1.5 hydrate [complex (1)] was prepared by a method similar to that described by Vaughn [8].

μ-[(ethylenediamine) chromium (III) dichloro (ethylenediamine)] chloride [complex (2)] was prepared as follows: a precalculated weight of $CrCl_3 \cdot 6H_2O$ in 100 ml of H_2O was placed in a beaker and calculated volumes of HCl were added. The beaker was kept in ice and a diluted solution of ethylenediamine was then added dropwise. The green solution obtained was heated for 2 h in a steam bath to complete the reaction, then the solution was heated at 80°C. The remaining solution

Table 2
Observed and calculated weight loss during the thermal decomposition of complex (1) and (2)

Complex	Observed weight loss (%)	Calculated weight loss (%)	
Complex (1)			
1st stage	10	9.9	Loss 1.5 mole H_2O
2nd stage	44.17	44	Loss 2 mole of ethylenediamine
Complex (2)			
1st stage	11.9	12.07	Loss 1 mole of ethylenediamine
2nd stage	24	24.145	Loss 2 mole of ethylenediamine

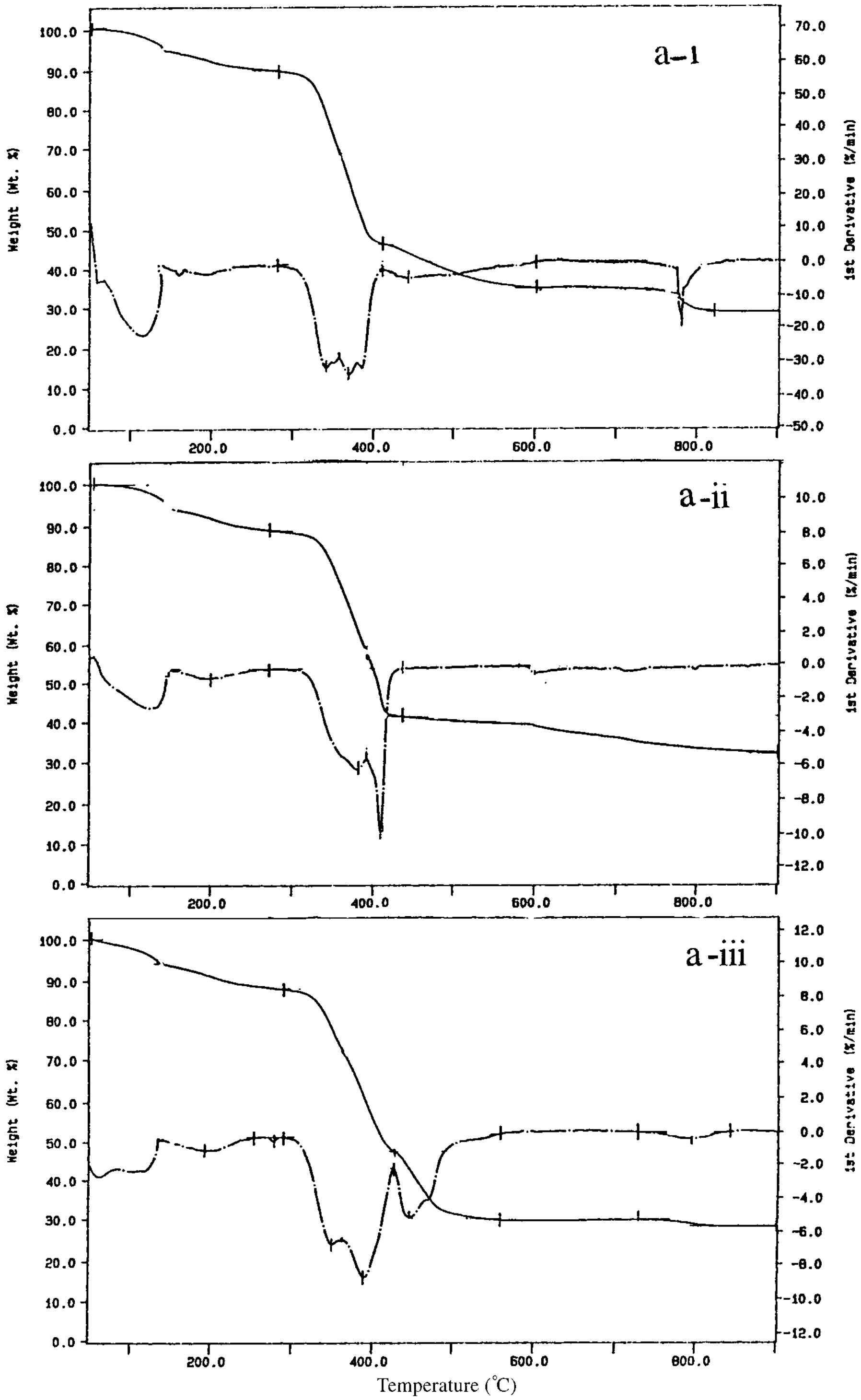

Fig. 2. (a)TG–DTG curves of complex (1) at heating rates (i) 5°C min^{-1}, (ii) 10°C min^{-1}, (iii) 15°C min^{-1} and (b) DTA at heating rate 10°C min^{-1}.

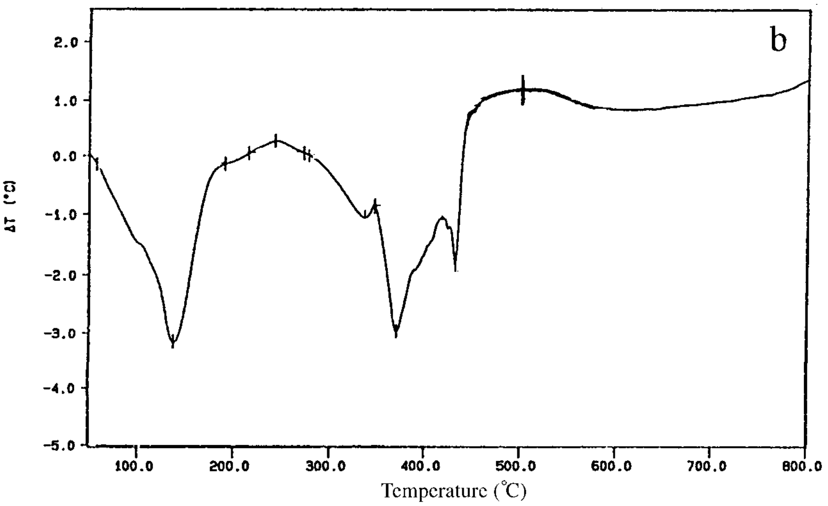

Fig. 2. (*Continued*).

was allowed to stand at room temperature till green crystals were preciptated and then was washed with ethanol and dried in air.

2.2. Apparatus

IR spectra were measured by Perkin Elmer spectrophotometer 1000 between 400 and 4000 cm^{-1}. Samples were prepared in the form of KBr disk.

Carbon, hydrogen and nitrogen were determined by Perkin Elmer 2400 CHN and chromium was determined by atomic absorption Perkin Elmer model 3100. TG and DTA were carried out using Perkin Elmer, 7 series thermal analysis system.

3. Results and discussion

The chemical analysis of the two solid complexes are shown in Table 1 which shows the similarity of experimental results with the theoretical content of the complexes. IR spectra for complex (1), Fig. 1, shows Cr–N strectching vibration at 460 cm^{-1} within the range reported by Hay [9]. Fig. 1 also shows bands at 3200 and 3107 cm^{-1} for NH_2 [10–12] and also a broad one at 3450 cm^{-1}for hydrated water [11] (lattice water). IR spectra for complex (2), Fig. 1 shows Cr–N band at 525 cm^{-1} [9] and bands at 3200 and 3070 cm^{-1} for NH_2 [10–12].

TG for the two complexes using different heating rates 5, 10 and 15°C min^{-1} and DTA are shown in Figs. 2 and 3 and the corresponding weight loss data are given in Table 2. Fig. 2 shows that the TG curves of complex (1) exhibit inflection points beginning at ~60°C due to the loss of water of hydration [1,3] (10%) and the formation of the anhydrous complex (*trans* $[Cr(en)_2F_2]Cl$) a second inflection point at ~250°C corresponding to the loss of two moles of ethylenediamine [1,3] (44.17%) and a third inflection point at ~430°C attributed to the formation of Cr_2O_3 [3]. TG data were confirmed by DTA measurements, Fig. 2 where three endothermic peaks located at 137°C due to the loss of hydrated water and a split peak at 337°C and 370°C attributed to the loss of two moles of ethylenediamine and an exothermic peak at 500°C due to the formation of Cr_2O_3. These results are in agreement with the weightloss data, Table 2. IR spectra for each stage of decomposition were measured, Fig. 4, which shows (i) a decrease in intensity of the broad band at 3450 cm^{-1} due to loss of hydrated water and (ii) the disappearance of the bands at 3200, 3107 and 469 cm^{-1} due to the loss of ethylenediamine entities together with the appearance of the band at 555 cm^{-1} attributed to ν(Cr–O) of Cr_2O_3.

TG analysis for complex (2) Fig. 3, shows inflection starting at ~190°C due to the loss of one mole of ethylenediamine (11.9%) a second inflection point at ~250°C corresponding to the loss of two moles of

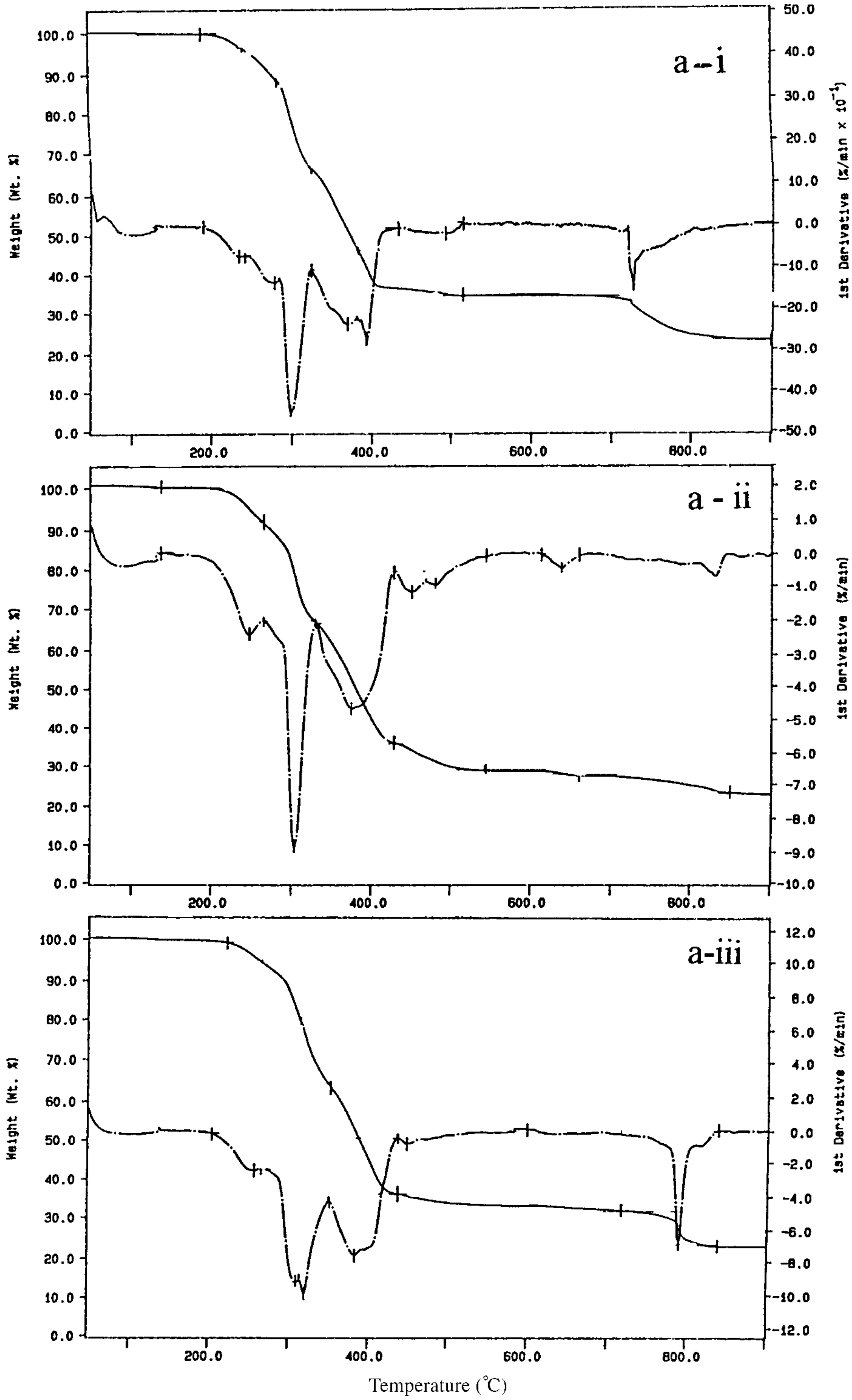

Fig. 3. (a) TG–DTG curves of complex (2) at heating rates (i) 5°C min^{-1}, (ii) 10°C min^{-1}, (iii) 15°C min^{-1} and (b) DTA at heating rate 10°C min^{-1}.

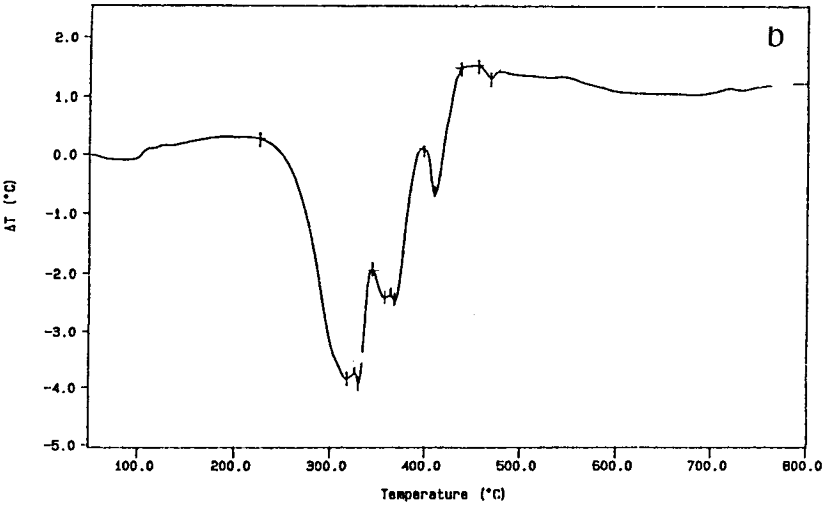

Fig. 3. (*Continued*).

ethylenediamine similar to complex (1) and a third inflection point at 500°C attributed to the formation of the oxide. These data were confirmed by DTA measurements, Fig. 3, where two endothermic peaks at 318°C were observed attributed to the loss of one mole of ethylenediamine and a split peak at 330°C and 370°C due to the loss of the other two moles of ethylenediamine in agreement with the weightloss data, Table 2. IR spectra for each stage of decomposition were measured and shown in Fig. 4. Fig. 4 shows the disappearance of the bands at 525, 3200 and 3070 cm^{-1} attributed to the loss of ethylenediamine and the appearance of a band at 590 cm^{-1} attributed to ν(Cr–O) of the oxide formed.

Arrhenius plots obtained from TG data are shown in Figs. 5 and 6 for the thermal decomposition of the two complexes, respectively. The non-isothermal plots were evaluated using Eq. (1) [13–16]:

$$\log\frac{(\mathrm{d}\alpha/\mathrm{d}T)\cdot\beta}{f(\alpha)} = \log k = \log A\frac{E}{2.303RT}, \quad (1)$$

where $\mathrm{d}\alpha/\mathrm{d}T$ is the fraction decomposed per degree, β the heating rate, $f(\alpha) = (1-\alpha)$, T the temperature in degree Kelvin, E the energy of activation, A the Arrhenius frequency factor and R the general gas constant.

Values of the energy of activations and Arrhenius frequency factors were evaluated from Arrhenius plots Figs. 5 and 6 and are given in Table 3.

First order kinetics were confirmed by applying Eq. (2) [3,17]:

$$\frac{\log(dw/dt)}{\log w_\mathrm{r}} = x - \frac{E/2.30R(1/T)}{\log w_\mathrm{r}}, \quad (2)$$

where $w_\mathrm{r} = w_\mathrm{l} - w_t$, w_l is the weightloss at the completion of the reaction, w_t that at time t and x the order of reaction. A plot of $\log(\mathrm{d}w/\mathrm{d}t)/\log w_\mathrm{r}$ vs. $(1/T)/\log w_\mathrm{r}$ yielded straight line, Fig. 7, with $x = 1$ for all the reactions studied, values of E, the energy of activation obtained from Eq. (2) are of the same order of magnitude as that given in Table 3. The data given in Table 3, indicate that the dehydration process for complex (1) follows evaporation mechanism, whereas, deamination which involves the break of Cr–N bond is rate determining for the two complexes.

Values of Δs^*, the entropy of activation, were calculated from the theory of absolute reaction rate, Eq. (3):

$$A = k\frac{T}{h}\mathrm{e}^{\Delta s*/R} \quad (3)$$

are also given in Table 3, which shows that the activated complex is less restricted in rotation [18,19] ($\Delta s^* < 1$) compared to the reactants for the dehydration and deamination of complex (1) at all heating rates and also for the first stage of deamination of complex (2) [18,19].

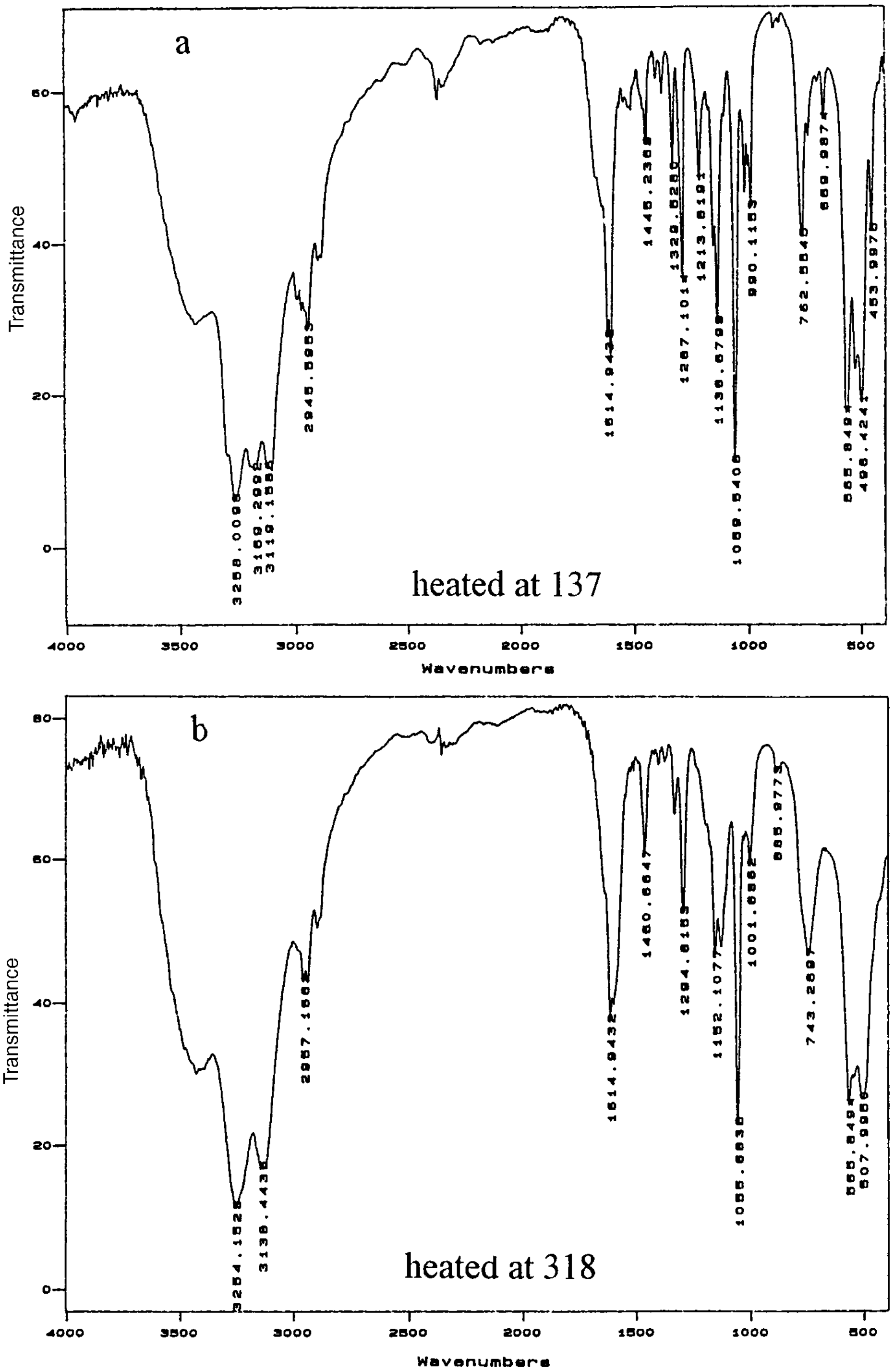

Fig. 4. IR spectra for the decomposition products of (a) complex (1) and (b) complex (2).

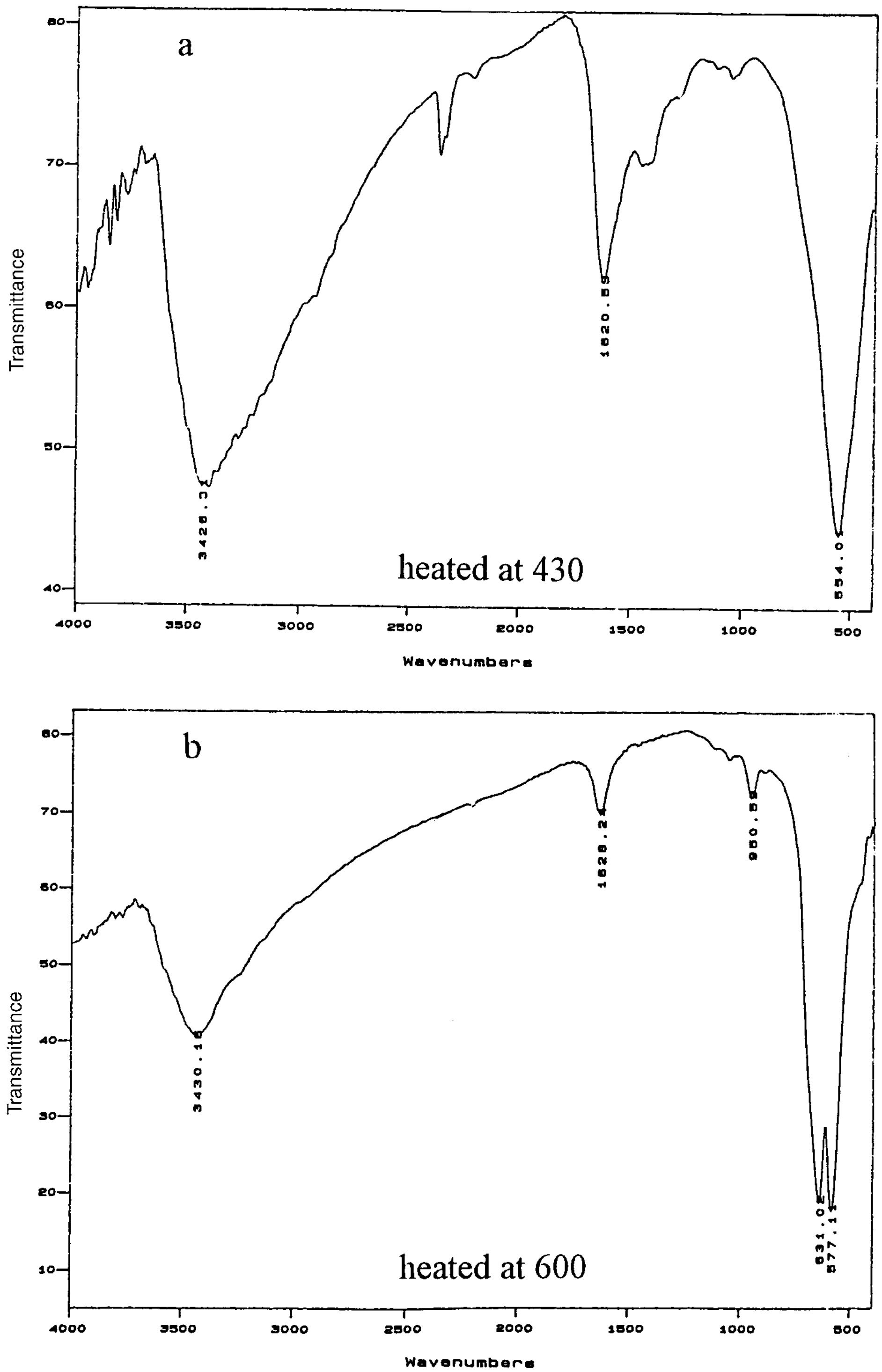

Fig. 4 (*Continued*).

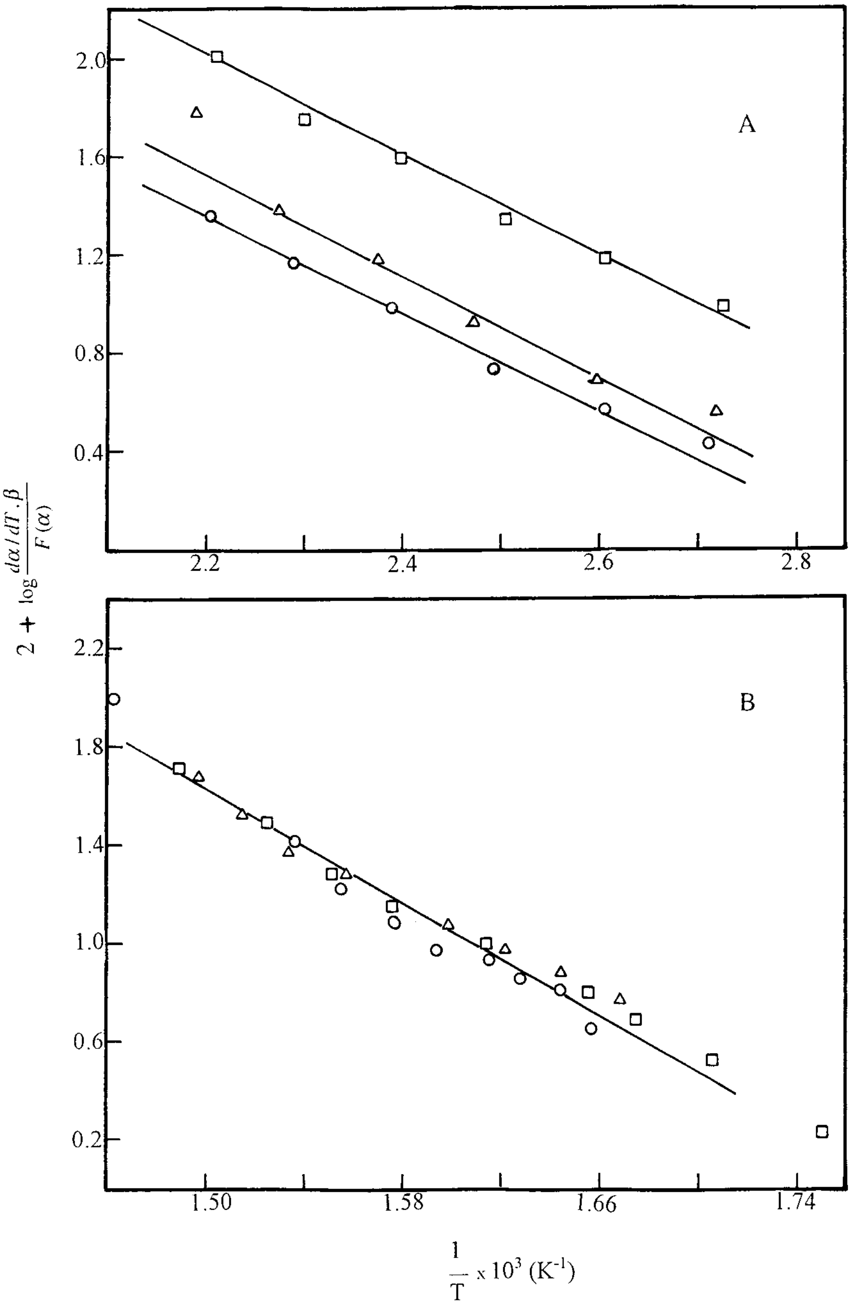

Fig. 5. Arrhenius plots for the non-isothermal, (A) dehydration and (B) deamination of complex (1) at heating rates, (○) 5°C min^{-1}; (Δ) 10°C min^{-1}; (□) 15°C min^{-1}.

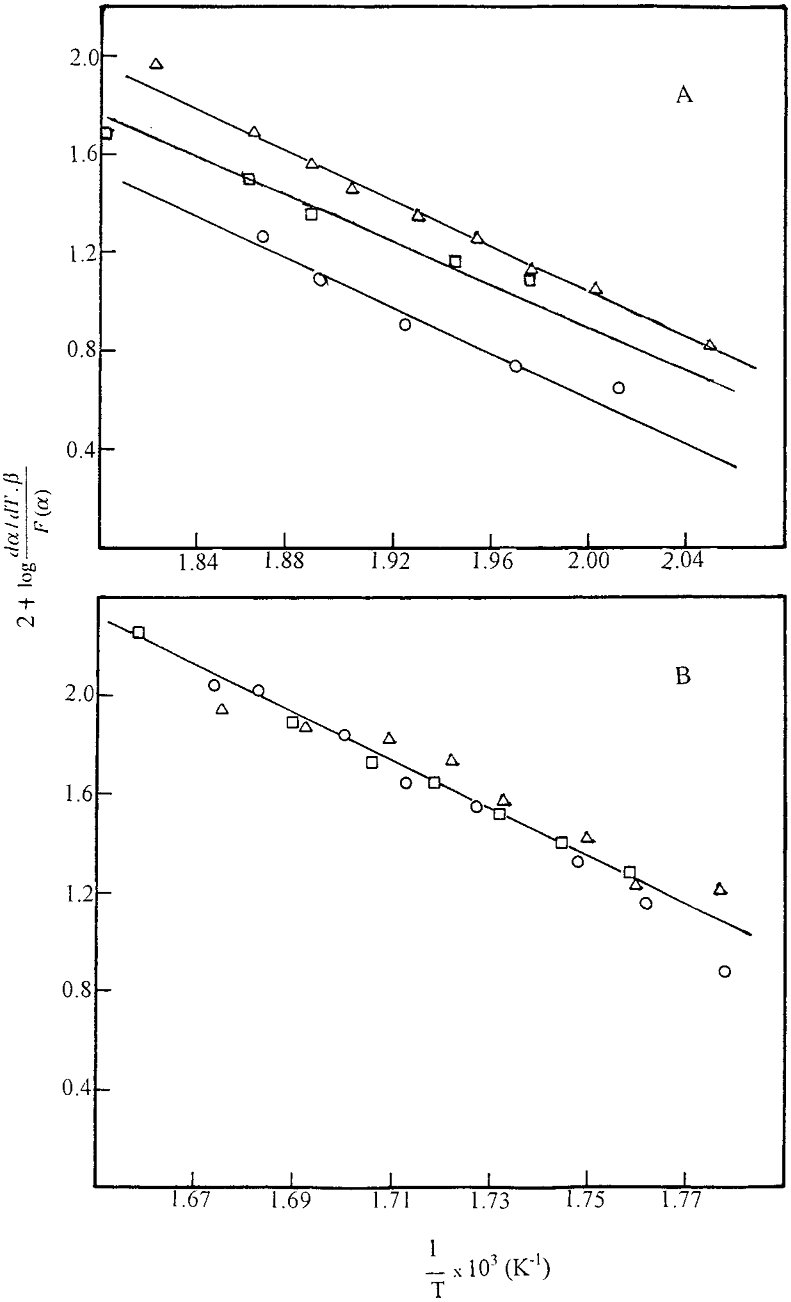

Fig. 6. Arrhenius plots for the non-isothermal deamination of complex (2) (A) the first stage, (B) the second stage at heating rates, (○) 5°C min^{-1}; (Δ) 10°C min^{-1}; (□) 15°C min^{-1}.

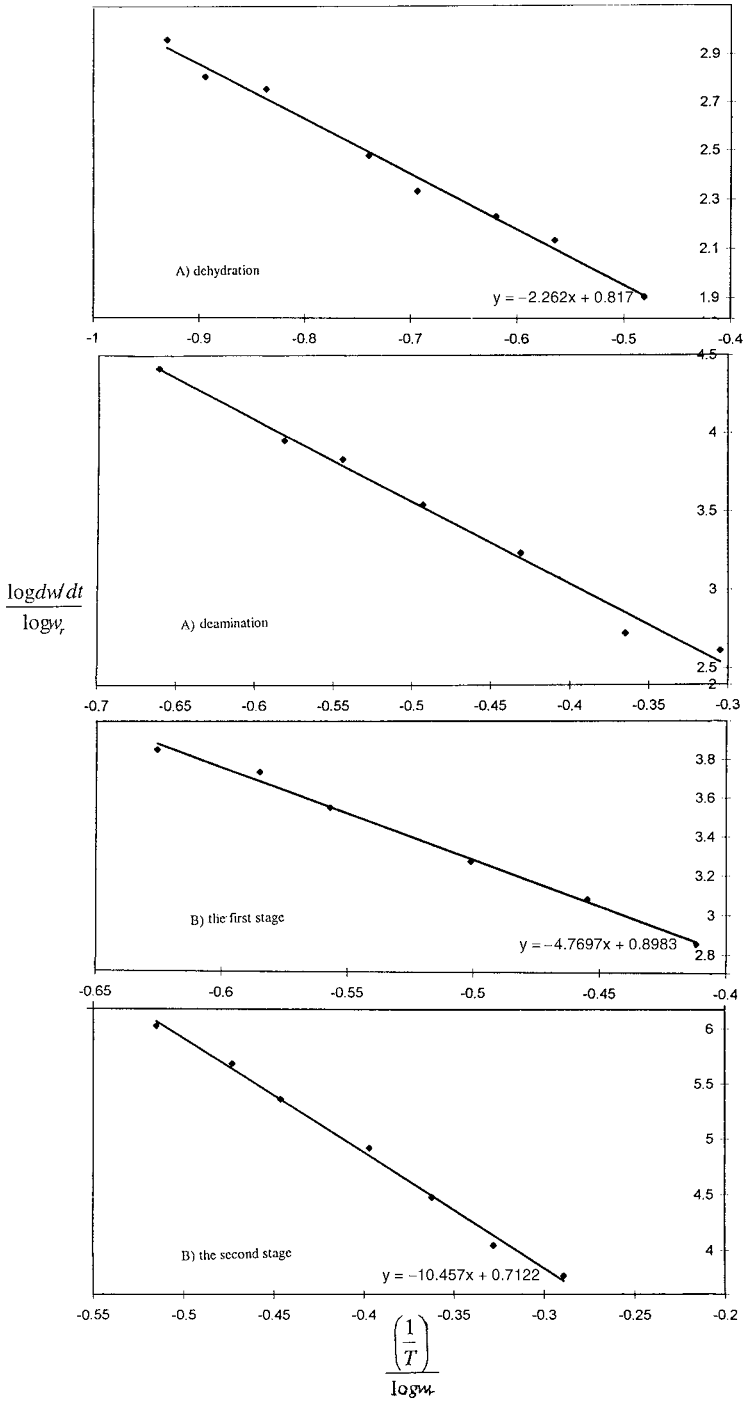

Fig. 7. Kinetics of the thermal decomposition of (A) complex (1) (B) Complex (2).

Table 3
Values of the Arrhenius parameters for the thermal decomposition of complex (1) and (2)

	Temperature (°C)	Kinetic parameter	Thermogravimetry		
			5°C min^{-1}	10°C min^{-1}	15°C min^{-1}
Complex (1)					
Dehydration	137	E (kJ mol^{-1})	38.2	38.1	38.6
		A (s^{-1})	95.9	196	494
		Δs^* (J K^{-1} mol^{-1})	−209.3	−203.3	−195.7
Deamination	370	E (kJ mol^{-1})	103.5	100.2	103.2
		A (s^{-1})	6.63×10^5	1.61×10^5	8.82×10^5
		Δs^* (J K^{-1} mol^{-1})	−139.4	−151.1	−137.0
Complex (2)					
Deamination, Stage (1)	318	E (kJ mol^{-1})	86.7	86.7	86
		A (s^{-1})	7.1×10^5	2.2×10^6	7.7×10^5
		Δs^* (J K^{-1} mol^{-1})	−148.0	−129.1	−135.3
Deamination, Stage (2)	345	E (kJ mol^{-1})	203	203	203
		A (s^{-1})	1.39×10^{15}	1.39×10^{15}	1.39×10^{15}
		Δs^* (J K^{-1} mol^{-1})	38.6	38.6	38.6

As for the second stage of deaminatin of complex (2) at all heating rates, values of Δs^*, Table 3, indicate high activity of escaping molecules by rotation of reactants on the surface and/or by formation of a mobile surface layer.

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