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THERMOCHEMICAL PARAMETERS OF THE THERMAL DEHYDRATION OF *TRANS*[CrF(H_2O)(1,3-DIAMINOPROPANE)$_2$][Ni(CN)$_4$]

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ABSTRACT

The solid state thermal dehydration of *trans*[CrF(H_2O)(tmd)$_2$][Ni(CN)$_4$] (tmd = 1,3-diaminopropane) has been investigated by means of DSC and TG measurements. The enthalpy of reaction was determined and the activation energy was found by non-isothermal and isothermal kinetic studies.

INTRODUCTION

In recent years the thermal dehydration reactions of coordination compounds especially of the type

$$[M(H_2O)(NH_3)_5]X_3 \rightarrow [M(X)(NH_3)_5]X_2 + H_2O$$

$$(M = Co, Cr, Ru; X = Cl, Br, I, NCS, NO_3^- \ldots)$$

have been studied thermochemically. The work of Wendlandt et al. [1–5] regarding new methods of complex synthesis and calculation of the thermodynamic and kinetic parameters of such reactions must be mentioned.

When $X = [M(CN)_6]^{3-}$ (M = Co, Cr, Fe) it is possible to apply the former reaction to the synthesis of new dinuclear compounds with a cyanide bridge.

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For example, the reaction

$$[Co(H_2O)(NH_3)_5][Co(CN)_6] \rightarrow [(NH_3)_5Co{-}NC{-}Co(CN)_5]$$

has been studied from the synthetical [6] and thermochemical [7,8] points of view. The resultant product has been characterized by X-ray diffraction [9], once purified by crystallization in aqueous solution. On the other hand, the same reaction has not allowed the isolation of definite compounds using other trivalent metals [10], since simultaneous reactions with a loss of water and ammonia (including HCN) are produced, causing very insoluble polymers. In spite of this, kinetic parameters for the different stages of the decomposition reaction when the cyanometallate is $[Cr(CN)_6]^{3-}$ and $[Fe(CN)_6]^{3-}$, have recently been obtained [11,12]. Considering this difficulty (loss of water and ammonia is simultaneous), the synthesis and characterization of several dinuclear complexes with a cyanide bridge, starting from several salts with ethylenediamine(en) or propylenediamine(tmd) ligand, whose chelate character gives them a great thermic stability, were attempted. The cations *trans*$[CrF(H_2O)(en)_2]^{2+}$ and *trans*$[CrF(H_2O)(tmd)_2]^{2+}$ being particularly stable, were specially considered. In fact, starting from these salts, a number of dinuclear complexes have been prepared and reported by us [13–16] using a similar method: the solid state dehydration reaction of the mixed salt complex prepared with several cyanometallates as anions. In one of these works [16] the synthesis and characterization of *trans*-$[CrF(H_2O)(tmd)_2][Ni(CN)_4]$, together with its thermal dehydration to *trans*$[(tmd)_2FCr{-}NC{-}Ni(CN)_3]$, were described.

Several solid state thermal studies have been described with 'en' or 'tmd' ligand, mainly the type $[Cr(amine)_3]X_3 \rightarrow [CrX_2(amine)_2]X$[17–19] or $[Cr(H_2O)_2(en)_2]X_3 \rightarrow [CrX_2(en)_2]X$ [20]. In this paper the solid state thermal dehydration results of trans$[CrF(H_2O)(tmd)_2][Ni(CN)_4]$ under non-isothermal and isothermal conditions are presented and the reaction mechanism is discussed.

EXPERIMENTAL

Preparation of trans$[CrF(H_2O)(tmd)_2][Ni(CN)_4]$

The salt may be prepared in the anhydrous and/or dihydrate form [16]. To obtain the anhydrous form, 1 g of $K_2[Ni(CN)_4]$ [21] was dissolved in 10 ml of water and the solution was passed through an Amberlite IR 20 in the NH_4^+ form. One g of finely ground *trans*$[CrF(H_2O)(tmd)_2](ClO_4)_2$ [22,23] was added with constant stirring to the ice-cold solution. The pink solid so formed was filtered, washed with ethanol and ether and dried.

Thermogravimetric studies

Thermogravimetric curves were obtained using a Perkin-Elmer model TGS-1 thermal gravimetric system at a rate of 10°C min^{-1}, in an atmosphere of nitrogen. The size of the samples ranged in mass from 5–6.5 mg. The isothermal rate measurements were analyzed over a temperature range of 383–408 K. All computations were carried out using a programmable calculator, and a linear regression analysis was used to compute slopes, intercepts and standard deviations.

Reaction enthalpy

Thermal dehydration studies were carried out using a Perkin-Elmer DSC-2 differential scanning calorimeter. Procedures were similar to those previously described [24].

KINETIC EQUATIONS

The activation energy was determined on the basis of a general kinetic relation. The reaction rate is expressed as the product of two functions, the former $k(T)$ dependent on the temperature, and the latter $f(x)$ on the x transformed fraction

$$dx/dt = k(T)\, f(x) \tag{1}$$

where $k(T)$ follows the Arrhenius law

$$k(T) = k_0 \exp[-E_a/RT] \tag{2}$$

with k_0 frequency factor and E_a activation energy.

If it is assumed that $f(x) = (1 - x)^n$, the activation energy E_a and the reaction order n may be obtained by non-isothermal and isothermal methods.

(1) *Non-isothermal method*: when the heating rate S is constant

$$\int_0^x \frac{dx}{(1-x)^n} = \frac{k_0}{S}\int_0^T \exp[-E_a/RT]\, dT \tag{3}$$

The right-hand side of eqn. (3) has no exact integral, but using the approximation of Coats and Redfern [26], eqn. (3), after taking logarithms, becomes

$$\ln\left[\frac{1-(1-x)^{(1-n)}}{T^2(1-n)}\right] = \ln\frac{k_0 R}{S\, E_a}\left[1 - \frac{2RT}{E_a}\right] - \frac{E_a}{RT} \tag{4}$$

for all values of n, except $n = 1$, in which case eqn. (3) becomes

$$\ln\left[-\ln\frac{(1-x)}{T^2}\right] = \ln\frac{k_0 R}{S\,E_a}\left[1 - \frac{2RT}{E_a}\right] - \frac{E_a}{RT} \tag{5}$$

(2) *Isothermic method*: integration of eqn. (1) gives

$$1-(1-x)^{1-n} = k(1-n)t \tag{6}$$

Equation (6) is the generalized rate equation for a reaction of order n. When $n = 1$, eqn. (1) yields the simple first order kinetics form

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

RESULTS AND DISCUSSION

(a) Non-isothermal TG

The TG curves for the solid state thermal dehydration of *trans*-$[CrF(H_2O)(tmd)_2][Ni(CN)_4]$ obtained at 10 K min^{-1} are shown in Fig. 1. A mass loss corresponding to a decrease in molecular weight of about 18 a.m.u. occurred at 408 K and a dark pink compound was obtained after the mass loss. The analyses and IR spectra obtained at the end of the first peak correspond to *trans*$[(tmd)_2FCr{-}NC{-}Ni(CN)_3]$, previously synthesized [16].

In order to characterize the TG curves obtained, the reaction order n, activation energy E_a, and pre-exponential factor k_0 have been derived using eqns. (4) and (5) for each run. The curves were analyzed assuming $n = 0$,

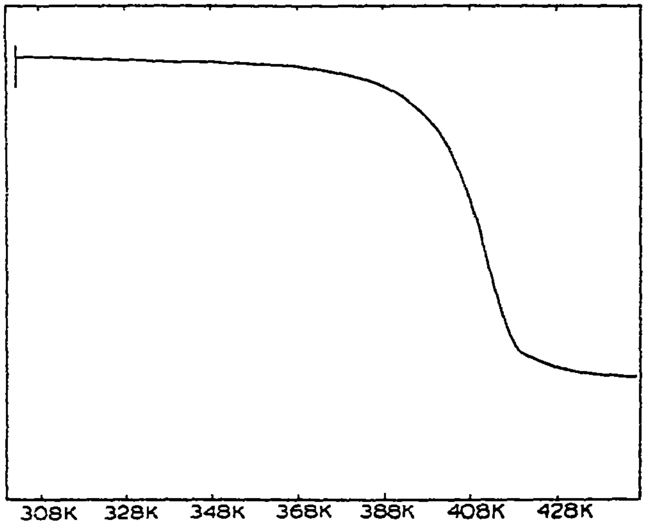

Fig. 1. TG curve of *trans*$[CrF(H_2O)(tmd)_2][Ni(CN)_4]$.

TABLE I

Numerical results of the TG curve of *trans*[CrF(H_2O)(tmd)$_2$][Ni(CN)$_4$]

		Sample					Average	Deviation
		1	2	3	4	5		
$n=0$	r^2	0.9992	0.9997	0.9997	0.9995	0.9995	0.9995	0.0002
	E_a	27.58	28.87	28.07	29.62	27.91	28.41	0.83
	k_0	3.8×10^{12}	1.1×10^{13}	5.2×10^{12}	2.3×10^{13}	4.6×10^{12}	9.5×10^{12}	
$n=1/3$	r^2	0.9985	0.9997	0.9995	0.9993	0.9987	0.9992	0.0005
	E_a	31.23	32.49	31.73	32.85	31.47	31.95	0.69
	k_0	2.3×10^{14}	2.1×10^{15}	2.1×10^{14}	1.4×10^{15}	4.6×10^{14}	9.2×10^{14}	
$n=1/2$	r^2	0.9975	0.9992	0.9991	0.9990	0.9986	0.9987	0.0007
	E_a	33.47	34.71	32.56	34.83	33.65	33.84	0.94
	k_0	6.1×10^{15}	2.8×10^{16}	1.4×10^{15}	1.3×10^{16}	5.7×10^{15}	1.3×10^{15}	
$n=2/3$	r^2	0.9973	0.9990	0.9987	0.9987	0.9987	0.9984	0.0007
	E_a	35.36	36.82	35.93	36.67	35.72	36.10	0.62
	k_0	9.4×10^{16}	4.2×10^{17}	1.1×10^{17}	1.3×10^{17}	8.1×10^{16}	1.7×10^{17}	
$n=3/4$	r^2	0.9961	0.9984	0.9982	0.9982	0.9972	0.9978	0.0009
	E_a	36.73	37.92	36.23	37.35	36.54	36.95	0.67
	k_0	4.0×10^{17}	1.7×10^{18}	1.5×10^{17}	4.4×10^{17}	3.2×10^{17}	6.0×10^{17}	
$n=1$	r^2	0.9917	0.9954	0.9960	0.9948	0.9950	0.9946	0.0016
	E_a	40.27	41.39	40.45	40.31	39.92	40.47	0.55
	k_0	3.7×10^{19}	1.5×10^{20}	3.3×10^{19}	1.8×10^{19}	2.4×10^{19}	5.2×10^{19}	

1/3, 1/2, 2/3, 3/4 and 1 to determine to what degree the order affects the derived kinetic parameters. Between $n = 0$ and $n = 0.1$, it was analyzed with an ad hoc program at 0.01 intervals. The best correlation coefficient was found for $n = 0$. The numerical analysis results of the curves in the range $0.1 \leqslant x \leqslant 0.8$ are presented in Table 1.

The data shown in Table 1 indicate some interesting features. Thus, the average correlation coefficients for several runs show that the best fit appears when the zero order equation is used. The $n = 0$ value corresponds to a uniform reaction occurring over the surface, with no contraction of the reaction interface area [25]. There is no considerable variation in the activation energy values for the samples when a given order is assumed. Thus, when $n = 0$ the mean activation energy is 28.4 kcal mole^{-1}, with a standard deviation of 0.83. Otherwise, the activation energy values are sensitive to the order of reaction, increasing when n increases. The frequency factor k_0 was calculated. For $n = 0$, we found $k_0 \sim 10^{12}$, a value intermediate among those given by Cordes [27] and Shannon [28] for decomposition reactions (10^5–10^{18}). Low and high values indicate, respectively, rigidly and flexibly activated complexes; the present case is therefore an intermediate one.

(b) Isothermal TG

A number of experiments were performed at various constant temperatures, not much higher than that at which the non-isothermal curves showed the first deflection from the base line.

The primary kinetic data (x vs. time) obtained for the isothermal dehydration are shown in Fig. 2. The rate constants were determined at different

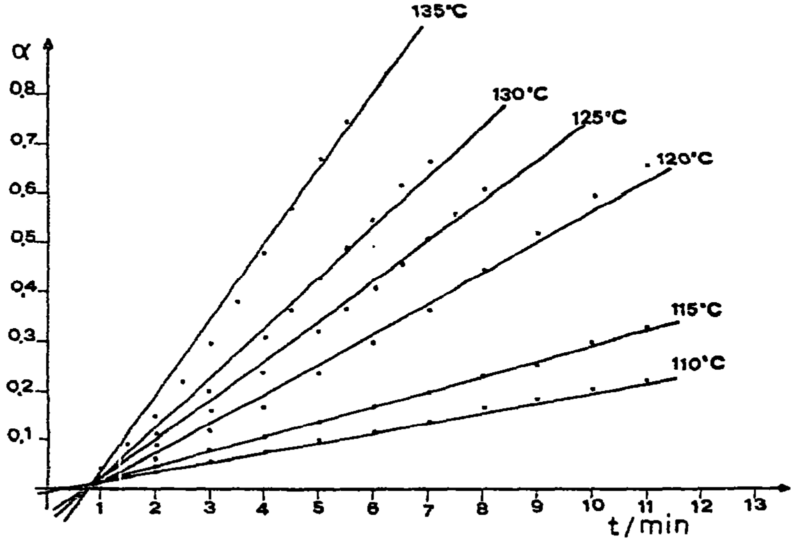

Fig. 2 Thermal dehydration of *trans*[CrF(H_2O)(tmd)$_2$][Ni(CN)$_4$] at different temperatures.

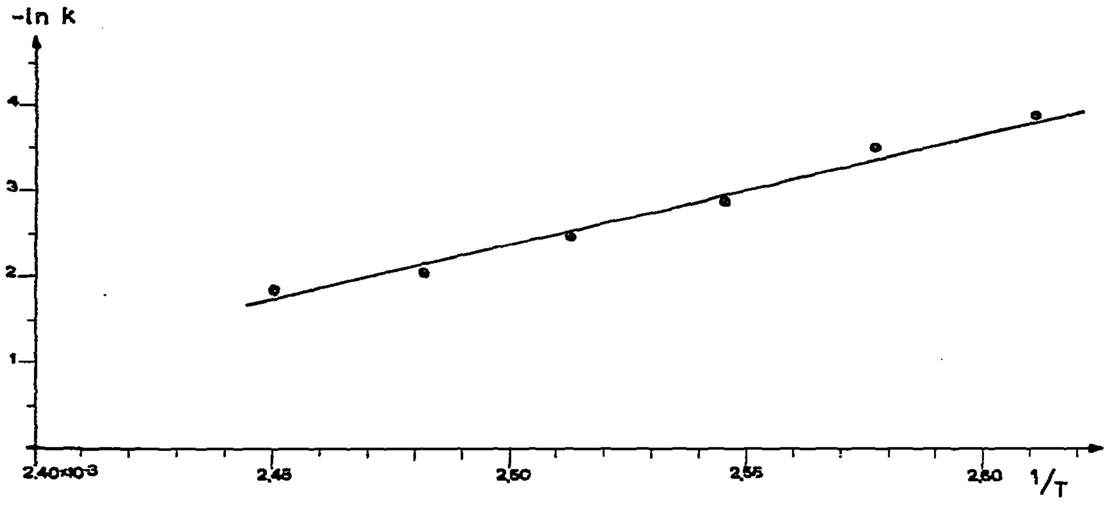

Fig. 3. Arrhenius plot, i.e. $-\ln k$ vs. $1/T$,

temperatures from the slopes of these lines, and thereafter the activation energy was calculated using an Arrhenius plot (Fig. 3). The value of E_a is 26.2 ± 3 kcal mole^{-1}. Kinetic dehydration parameters derived from non-isothermal kinetic studies were found to be consistent with the results obtained from isothermal methods.

(c) DSC

Analysis of the DSC curves in the dehydration region yields an activation energy of 28.0 ± 3 kcal mole^{-1} using the Thomas and Clarke method [29], and the enthalpy change for this process is 12.5 ± 1 kcal mole^{-1}. The E_a value obtained using DSC agrees with those obtained thermogravimetrically.

Possible mechanism

It is very difficult from E_a data to make definite conclusions regarding a possible mechanism. House [30] has recently proposed several mechanisms for the thermal dehydration reactions of solid complexes. He states that the chemical behaviour in solid dehydration is often determined by various types of defects: (a) Schottky defect, which is produced by the anion displacement over the cation, creating a local and momentary heptacoordination and a vacancy in the crystalline net. This will be an SN_2 associative mechanism; (b) Frenkel defect, which is produced by a loss of coordination water which is displaced to a net interstice creating a local and momentary pentacoordination. This will be an SN_1 dissociative mechanism. House has shown [30] that high values of E_a have a better correspondence to an SN_2 mechanism while low values have a better correspondence to SN_1.

In an SN_2 reaction, the formation of a seven-bond complex, based on a crystal field model, requires about 4.25 D_q [31] (with D_q being about 2025 cm^{-1} for the *trans* $[CrF(H_2O)(tmd)_2]^{2+}$) which alone would be about 25 kcal $mole^{-1}$, similar to the E_a found. However, considering that in the SN_2 reaction, the heptacoordination suggests, moreover, a Schottky defect formation in an ionic crystal, it requires high energy ($E_s = 0.4\ E_1$) [32] (E_1 = lattice energy). The 25–28 kcal $mole^{-1}$ value found is relatively low (compared with the value of about 60 kcal $mole^{-1}$ found for the dehydration of *trans*$[CrF(H_2O)(tmd)_2]\ S_2O_6$ [24]).

It is likely, therefore, that we have an SN_1 dissociative mechanism reaction with the formation of a square-pyramid activated complex requiring only $2D_q$ [31]; that is, the transition state is determined by the water loss and a non-ionic Frenkel defect formation. This implies no variation of E_a regarding similar anions, in which, a priori, the mechanism would be identical. In the near future we intend to verify this with $[Pd(CN)_4]^{2-}$ and $[Pt(CN)_4]^{2-}$ ions.

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