

KINETIC PARAMETERS AND SOLID STATE MECHANISM OF THE THERMAL DEHYDRATION OF $trans|CrF(H_2O)(en)_2|I_2$, $trans|CrF(H_2O)(tn)_2|I_2 \cdot H_2O$ and $trans|CrF(H_2O)(en)(tn)|I_2 \cdot H_2O$ (en = ETHYLENEDIAMINE; tn = 1,3-DIAMINOPROPANE)

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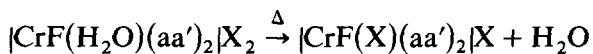
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ABSTRACT

The solid phase thermal deaquation-anation of $trans|CrF(H_2O)(en)_2|I_2$, $trans|CrF(H_2O)(tn)_2|I_2 \cdot H_2O$ and $trans|CrF(H_2O)(en)(tn)|I_2 \cdot H_2O$ (en = ethylenediamine; tn = 1,3-diaminopropane) has been investigated by means of isothermal and non-isothermal TG measurements. The kinetic parameters have been found by isothermal studies; the physical model of these reactions (nucleation, growth or intermediates) has been found by the shapes of the isothermal curves and by comparison of the isothermal and non-isothermal data for all the principal $g(\alpha)$ expressions. Values found for activation energy are low (about 130 kJ mol⁻¹ for the en compound; about 70 kJ mol⁻¹ for the tn compound, and about 110 kJ mol⁻¹ for the mixed en-tn compound). These data permit the assignment of the deaquation-anation mechanism as S_N1 type, involving a square-base pyramid activated complex and elimination of water as Frenkel defects.

INTRODUCTION

Reactions of the type



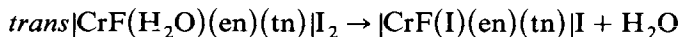
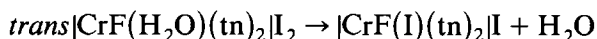
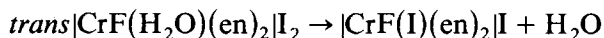
(aa' = ethylenediamine or 1,3-diaminopropane) have been widely studied by Vaughn et al. [1-3]. The principal aim of these works was, nevertheless, purely preparative and not a systematization of thermodynamic and/or kinetic parameters of the solid state reaction. It only shows the ease or difficulty of an entering ligand X from the temperature at which the anation reaction took place. So, for aa' = en, the anation temperature follows the order I⁻ > Br⁻ > Cl⁻.

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Surprisingly, in spite of the great stability of the Cr–N bond in these chelating ligands, in the literature only a few kinetic studies of the dehydration–anation of chromium(III) salts with the less stable NH_3 ligand are found. In particular, these studies have been made by Wendlandt and co-workers since 1959 [4].

It was understood, nevertheless, that the mechanism is practically the same. Literature data concerning such mechanisms show that the activation energies for these reactions vary with the anion. This apparent anion effect has been attributed to an $\text{S}_{\text{N}}2$ (or associative mechanism) ligand exchange between the departing H_2O and the entering anion X. However, for the same substances, the activation parameters reported by different authors are in poor agreement. According to LeMay and Babich [5] this is due to the fact that the experimental conditions have not been specified or controlled. Thus, as LeMay points out, when procedural variables are held constant, activation parameters for different salts agree within experimental error. This could mean, according to the House theory [6], that an $\text{S}_{\text{N}}1$ (dissociative) rather than an $\text{S}_{\text{N}}2$ mechanism is involved in the ligand exchange process. If an $\text{S}_{\text{N}}1$ mechanism is supposed, explained in terms of the formation of Frenkel defects by elimination of water molecules [6], the activation energy must be dependent on the relative size of ions; that is, according to the difference between size of the cation and anion, the water molecule may be more or less able to slip into an interstitial position and escape from the crystal.

For this reason and taking into account the fact that the ethylenediamine ligand is smaller than the tn ligand, and that the cation with en–tn ligands should be an intermediate case in its size, in the present work an attempt is made to study the kinetic parameters of the reactions



(en = ethylenediamine; tn = 1,3-diaminopropane).

Other compounds with en and/or tn ligands have been studied by the authors previously; the entering anions were cyano-complexes [7–9].

EXPERIMENTAL

Preparation of the compounds

Trans $[\text{CrF}(\text{H}_2\text{O})(\text{en})_2]\text{I}_2$ was prepared as described in the literature [1], but in the anhydrous form and not with 0.5 mol of water, as previously reported [1]. *Trans* $[\text{CrF}(\text{H}_2\text{O})(\text{tn})_2]\text{I}_2 \cdot \text{H}_2\text{O}$ was synthesized as the en analogue from $[\text{CrF}(\text{H}_2\text{O})(\text{tn})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ [2]. *Trans* $[\text{CrF}(\text{H}_2\text{O})(\text{en})(\text{tn})]\text{I}_2 \cdot$

H₂O is a new compound synthesized by the authors [10] from [CrF₂(H₂O)₂-(en)]Br [11].

Analyses of Cr, I, C, H, and N agree with the formulae proposed. Previous TG curves also indicate 1 mol of water of crystallization in the tn case, the two other cases being anhydrous.

TG studies

Thermogravimetric studies were carried out on a Perkin-Elmer TGS-1 system in an atmosphere of nitrogen. Non-isothermal measurements were made at a rate of 5°C min⁻¹; 6–7 mg of sample were used. The kinetic parameters were determined on the basis of the general kinetic relation

$$d\alpha/dt = k(T) \cdot f(\alpha)$$

where $k(T) = K_0 \exp[-E_a/RT]$ (Arrhenius law); K_0 = frequency factor; E_a = activation energy; and α = mole fraction. Mathematically, this expression can be converted to

$$\int_0^1 d\alpha/f(\alpha) = \int_{T_0}^{T_1} k(T) dt, \text{ being } \int_0^1 d\alpha/f(\alpha) = g(\alpha)$$

The main difficulty in solid kinetics is the determination of the appropriate expression of $g(\alpha)$ or $f(\alpha)$.

In the present work all the principal expressions of $g(\alpha)$ indicated in the literature [12] have been used, following the four physical models of solid state chemistry: nucleation, growth, nucleation-growth and diffusion. The truer activation energy was determined by a series of isothermal TG curves which gave a value of E_a almost independent of the physical model proposed. In order to determine the more likely solid state model this value has been compared with the variable values obtained with non-isothermal measurements. In the non-isothermal measurements the expression $g(\alpha) = \int k(T) dt$ was resolved by the widely employed approximation of Coats and Redfern [13]. For isothermal analysis the general equation is simply $g(\alpha) = kt$. In this case, an isothermal preheating at low temperature (50–60°C) was made to eliminate the external and crystallization water, until the weight remained stable.

RESULTS AND DISCUSSION

The non-isothermal TG curve for the solid phase thermal deaquation of *trans*[CrF(H₂O)(tn)₂]I₂ · H₂O is given in Fig. 1. A mass loss of approximately 18 a.m.u. occurs between room temperature and 90°C, corresponding to the water of crystallization. Effectively, if the process is stopped at 80–90°C or if preheating to the isothermal temperature (50°C) until con-

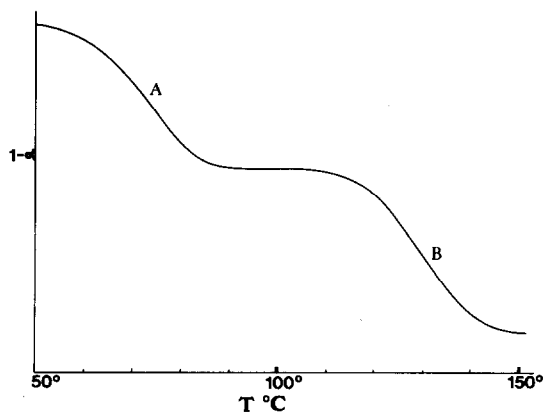


Fig. 1. Non-isothermal TG curve of $\text{trans}[\text{CrF}(\text{H}_2\text{O})(\text{tn})_2]\text{I}_2 \cdot \text{H}_2\text{O}$. (A and B = crystallization and coordination water, respectively.)

stant weight is carried out, the compound so obtained has the same UV-visible and IR spectra as the starting product. Between 100 and 150°C there is a second mass loss corresponding to a molecular weight decrease of 18 a.m.u. and a new compound was observed at the end of the curve which corresponds to $[\text{CrF}(\text{I})(\text{tn})_2]\text{I}$, according to spectroscopic measurements [10].

The isothermal TG curves were obtained at five different temperatures for each product. The results for the $\text{trans}[\text{CrF}(\text{H}_2\text{O})(\text{tn})_2]\text{I}_2 \cdot \text{H}_2\text{O}$ (preheated isothermally at 50°C in the same TG apparatus until constant weight, in order to eliminate the water of crystallization) are given in Fig. 2. The

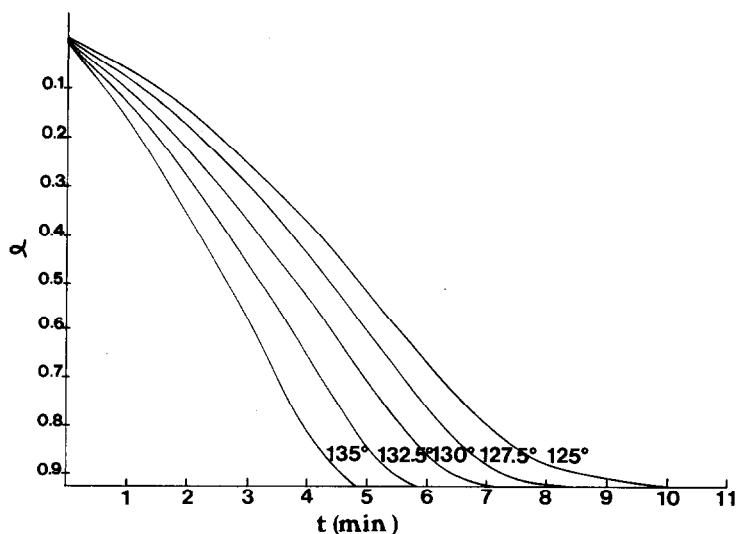


Fig. 2. Isothermal TG curves for $\text{trans}[\text{CrF}(\text{H}_2\text{O})(\text{tn})_2]\text{I}_2$ (preheated at 50°C until constant weight). The curves are cut at $\alpha = 0.9$ in order not to lengthen the abscissa (to arrive at $\alpha = 1$ it may be necessary to heat at 125°C for approximately 30 min).

non-isothermal TG curves for the other two compounds are very similar to that shown in Fig. 1, but without the first step corresponding to the water of crystallization. Also there is a change in the starting and final temperatures: from 150 to 210°C for the en compound; from 110 to 150°C for the tn compound (Fig. 1), and from 140 to 200°C for the mixed en-tn compound. The isothermal TG runs for these other two products are also very similar but less sigmoid and are not indicated here (Fig. 2).

In order to calculate the kinetic parameters, all the principal expressions of the solid state decompositions are used (Table 1) both in isothermal and non-isothermal measurements (see Experimental).

The results obtained for the new compounds are given in Tables 2-5. The computation for each $g(\alpha)$ and for each n has been carried out with an ad hoc FORTRAN IV program. Taking into consideration that all the dehydration-anation processes of amino-complexes of chromium(III) are never described in terms of diffusion law, we could expect that these new compounds behave according to the growth, nucleation or nucleation-growth laws. Effectively, the E_a , k_0 and r^2 values found by us with the diffusion model are inconsistent when comparing the non-isothermal and isothermal measurements [14]. Therefore, in Tables 2-4 only the values found for each compound from the growth, nucleation and nucleation-growth models are reported. For brevity and in order to indicate only the most prominent features, only the kinetic parameters for a few n values are given in each Table (in fact, these parameters were calculated for more n values [14]). It is known from the literature [15,16] that this apparent order, n , does not have to be integral but may be also a decimal number.

TABLE 1

Kinetic functions, $g(\alpha)$, used in their integral form

Mechanism	$g(\alpha)$
<i>Nucleation controlled</i>	
Exponential law	$\ln \alpha^n$
Power law	$\alpha^{1/n}$
<i>Growth controlled</i>	
For $n = 1$	$[1 - (1 - \alpha)^{1-n}] / (1 - n)$ $[-\ln(1 - \alpha)]$
<i>Nucleation - growth controlled</i>	
Avrami-Erofeev	$[-\ln(1 - \alpha)]^{1/n}$
Prout-Tompkins	$\ln[\alpha / (1 - \alpha)]$
<i>Diffusion controlled</i>	
One-dimensional	α^2
Two-dimensional	$\alpha + (1 - \alpha)\ln(1 - \alpha)$
Three-dimensional	$[1 - (1 - \alpha)^{1/3}]^2$
Three-dimensional	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3}$

TABLE 2
Computational kinetic parameters for *trans*-CrF(H₂O)(en)₂II₂

	Mechanism								
	Growth model		Nucleation-growth (Avrami-Erofejev)		Nucleation (Power law)				
	<i>n</i> = 0	0.2	0.4	<i>n</i> = 1.0	1.5	2.0	<i>n</i> = 0.8	0.9	1.0
Non-isothermal measurements									
<i>E_a</i> (kJ mol ⁻¹)	131.8	141.9	152.8	189.5	123.8	90.9	166.6	147.3	131.8
<i>k₀</i> = 10 ^x	14	16	17	21	14	10	18	16	14
<i>r</i> ²	0.9820	0.9866	0.9903	0.9971	0.9970	0.9969	0.9824	0.9822	0.9820
Isothermal measurements									
<i>E_a</i> (kJ mol ⁻¹)	133.7	134.3	135.0	137.6	136.2	135.7	134.1	134.0	133.6
<i>k₀</i> = 10 ^x	15	15	15	16	15	15	15	15	15
<i>r</i> ²	0.9864	0.9738	0.9547	0.8897	0.9724	0.9851	0.9710	0.9800	0.9864

TABLE 3
Computational kinetic parameters for *trans*-(CrF(H₂O)(tn)₂)I₂

	Mechanism								
	Growth model		Nucleation-growth (Avrami-Erofev)		Nucleation (Power law)				
	$n = 0$	0.2	$n = 1.0$	2.0	3.0	3.5	$n = 1.5$	2.0	2.5
Non-isothermal measurements									
E_a (kJ/mol ⁻¹)	172.6	187.3	256.2	124.3	80.9	68.4	112.9	83.0	65.1
$k_0 = 10^x$	22	24	33	16	10	8	14	10	8
r^2	0.9845	0.9886	0.9908	0.9979	0.9978	0.9978	0.9839	0.9832	0.9825
Isothermal measurements									
E_a (kJ mol ⁻¹)	69.3	68.6	66.0	68.4	69.3	69.8	69.8	69.9	70.0
$k_0 = 10^x$	9	9	9	9	9	9	9	9	9
r^2	0.9902	0.9858	0.9618	0.9955	0.9984	0.9993	0.9918	0.9911	0.9908

TABLE 4
Computational kinetic parameters for *trans*-CrF(H₂O)(en)(tn)]₂

	Mechanism												
	Growth model												
	Nucleation-growth (Avrami-Erofev)		Nucleation (Power law)		Nucleation-growth (Avrami-Erofev)		Nucleation (Power law)		Nucleation-growth (Avrami-Erofev)		Nucleation (Power law)		
	<i>n</i> = 0	0.2	0.4	0.4	<i>n</i> = 1.0	1.5	2.0	<i>n</i> = 0.9	1.0	1.5	<i>n</i> = 0.9	1.0	1.5
Non-isothermal measurements													
<i>E_a</i> (kJ mol ⁻¹)	108.1	116.9	126.3	126.3	158.3	103.1	75.4	121.0	108.1	69.6	121.0	108.1	69.6
<i>k₀</i> = 10 ^{<i>x</i>}	12	13	14	14	18	12	8	14	12	7	14	12	7
<i>r</i> ²	0.9940	0.9965	0.9980	0.9980	0.9987	0.9976	0.9970	0.9941	0.9940	0.9935	0.9941	0.9940	0.9935
Isothermal measurements													
<i>E_a</i> (kJ mol ⁻¹)	110.0	110.7	110.9	110.9	112.3	110.8	108.6	113.0	113.2	112.6	113.0	113.2	112.6
<i>k₀</i> = 10 ^{<i>x</i>}	13	14	14	14	15	14	14	13	13	13	13	13	13
<i>r</i> ²	0.9903	0.9884	0.9865	0.9865	0.9843	0.9927	0.9936	0.9887	0.9903	0.9947	0.9887	0.9903	0.9947

TABLE 5

Average kinetic parameters calculated for the deaquation-anation reaction (see text for the model proposed)

Compound	E_a (kJ mol ⁻¹)	k_0
<i>trans</i> CrF(H ₂ O)(en) ₂ I ₂	130 ± 6	0.75 × 10 ¹⁵
<i>trans</i> CrF(H ₂ O)(tn) ₂ I ₂	70 ± 3	0.54 × 10 ⁹
<i>trans</i> CrF(H ₂ O)(en)(tn) I ₂	110 ± 3	0.66 × 10 ¹⁴

From Tables 2–4 it is seen that E_a and k_0 can be deduced from the isothermal curves, since the values so obtained are almost independent of the physical model proposed.

The kinetic parameters E_a and k_0 are given in Table 5. Taking into account the possible deviation and error of these values we can affirm that the true activation energy of the tn complex (about 70 kJ mol⁻¹) is somewhat lower than the activation energy of the en complex (about 130 kJ mol⁻¹); the mixed en–tn complex has an intermediate value (about 110 kJ mol⁻¹). Comparing the data of the activation energy of the other compounds previously reported by us in the series *trans*|CrF(H₂O)(tn)₂|M(CN)₄ (M = Ni, Pd, Pt) (E_a about 110 kJ mol⁻¹) [7,8]; *trans*|CrF(H₂O)(tn)₂|K|CrX(CN)₅ · H₂O (X = NO, CN) (E_a about 80 kJ mol⁻¹) [9]; *trans*|CrF(H₂O)(en)₂|M(CN)₄ (M = Ni, Pd, Pt) (E_a about 130 kJ mol⁻¹) [10] and *trans*|CrF(H₂O)(en)₂|K|CrX(CN)₅ · H₂O (X = NO, CN) (E_a about 100 kJ mol⁻¹) [9], it is seen that the tn complexes have a higher activation energy when they are anhydrous (from 110 kJ mol⁻¹ to 70 kJ mol⁻¹, when hydrated). The en complexes present a similar behaviour (from 130 kJ mol⁻¹ anhydrous to about 100 kJ mol⁻¹ monohydrate).

The difference between en, tn and en–tn mixed complex, and the apparent dependence of the water of crystallization will be discussed under Chemical Mechanism.

The values of k_0 indicate the rigidity of the activated complex. According to Cordes [17] and Shannon [18] the frequency factor may be related to the degrees of freedom of the activated complex and may vary between approximately 10⁵ and 10¹⁸. Small values often indicate a rigid activated complex without degrees of freedom and high values indicate a flexible activated complex. The three cases considered here (Table 5) are intermediate (10⁹ for the tn compound; 10¹⁵–10¹⁶ for the en complex; and 10¹⁴ for the en–tn complex). The complexes which contain en have a very similar value, greater than the tn complex.

This is accepted or assumed by many investigations with regard to the physical model or solid state mechanism, i.e., the function $g(\alpha)$ or $f(\alpha)$, overall with non-isothermal methods. In order to avoid assumptions, we consider that the solid state mechanism may be established by comparing the

dynamic and isothermal conditions, as also suggested by other authors [19,20], and using a good value of r^2 and the shape of the TG isothermal runs [12]. The advantage of this method is nothing is assumed about the mechanism, but all the kinetic parameters are determined from experimental results.

In the three cases studied here, the comparison is not unequivocal: in the en compound there is good agreement for the Avrami law with $n = 1.5$ or for the growth model with $n = 0$ (which mathematically equals the power law with $n = 1$; the Avrami model has a lower r^2). In the tn compound there is a good agreement for the Avrami law with $n = 3.5-4$ and also with the power law with $n = 2.5$ (lower r^2). There is no agreement for the growth model. Finally, in the en–tn mixed compound there is the same agreement as with the en complex (Tables 2–4).

Due to the sigmoid shape of the isothermal curves in the three compounds, especially in the tn compound, it is probable that the physical model corresponds to the nucleation–growth model, according to the Avrami law. The literature indicates that the sigmoid shape agrees with the Avrami law; the greater the sigmoid the higher the n value. In our case, with the tn ligand the shape of the curve is very sigmoid and agrees with $n = 3-3.5$; whereas the sigmoid shape of the en and en–tn compounds is less pronounced and corresponds approximately to $n = 1-1.5$.

CHEMICAL MECHANISM

House [6] has recently proposed several mechanisms in the thermal dehydration reaction of solid complexes, determined by various types of defects: Schottky defects with an S_N2 associative mechanism or Frenkel defects with an S_N1 dissociative mechanism. According to this theory, high values of E_a correspond better to an S_N2 mechanism while low values correspond better to S_N1 . In our case, in an S_N2 reaction, the formation of a seven-bond activated complex (pentagonal bipyramid) based on the crystal field model requires $4.26 Dq$ [21] (Dq being about 25 kJ mol^{-1}) for the aquoamine complexes of chromium(III), which alone would be about 105 kJ mol^{-1} , greater than the E_a found in at least two cases (Table 5). If the activated complex was an octahedral wedge, the energy required would be only $1.8 Dq$ (nearly 50 kJ mol^{-1}). However, considering that in the S_N2 reaction the hepta-coordination suggests a Schottky defect formation in an ionic crystal, it requires a high energy ($E_{Sch.} = 0.35 U$, where U is the lattice energy) [22]. Consequently, we would find a value greater than 130 kJ mol^{-1} .

It is likely, therefore, that we have an S_N1 (dissociative mechanism) with the formation of a square pyramid activated complex, requiring only $2 Dq$ [21] (activation energy about 50 kJ mol^{-1}) (for a trigonal bipyramid activated complex it would require $5.7 Dq$, i.e., 145 kJ mol^{-1} , greater than the E_a

found). Consequently, the transition state is determined by the water loss and a non-ionic Frenkel defect formation. The marked difference between the activation energies of $trans[CrF(H_2O)(en)_2]I_2$, $trans[CrF(H_2O)(tn)_2]I_2 \cdot H_2O$ and $trans[CrF(H_2O)(en)(tn)]I_2 \cdot H_2O$ (Table 5) is also a proof of the dissociative mechanism, the water loss being the more important step of the reaction. The water will be able to escape into the interstitial sites of the lattice when the free space in the net is greater. Evidently we can expect that the free space will be greater with the larger tn ligand than with the en ligand. For this reason the activation energy of complexes with tn is lower than that with en; when both ligands are present an intermediate case arises and, consequently, the activation energy is also intermediate (Table 5).

The last aspect to consider is the role of the water of crystallization. This water evidently expands the lattice with respect to the possible anhydrous compound. When this water is eliminated by isothermal preheating, the ions in the lattice are not completely rearranged; then, the free space left by this water molecule remains in the net. The coordination water will now have more facility to escape into these "new interstices" and the E_a will be lower. This hypothesis should be supported by other facts; this problem will be the subject of further studies.

In conclusion, the E_a found for the en and en-tn complexes are comparable since both are anhydrous; the E_a found for the tn complex is perhaps lower than the true value if the complex was anhydrous. In any case, the sequence for the E_a of the three compounds seems logical and supports the conclusion that the mechanism of these dehydration-anation reactions may be considered as dissociative (S_N1) with a square pyramid activated complex and an activation energy of approximately 70–130 kJ mol⁻¹.

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