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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)]

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ABSTRACT

The solid phase thermal deaquation–anation of isostructural $[M(H_2O)(NH_3)_5][Co(CN)_6]$ salts [M = Co(III), Rh(III) and Ir(III)] has been investigated by means of isothermal and non-isothermal TG measurements. The physical model of these reactions (nucleation–growth according to the Avrami–Erofeev law) has been found by comparison of the isothermal and non-isothermal TG data for all the principal $g(\alpha)$ expressions ($0.2 \leqslant \alpha \leqslant 0.8$) and by the shape of the isothermal curves. The values found for the activation energy are low (about 130 kJ mol^{-1} for the Co compound; approximately 110 kJ mol^{-1} for the Rh compound and about 95 kJ mol^{-1} for the Ir compound). These data permit the assignment of the deaquation–anation mechanism of the S_N1 dissociative type, involving square based pyramid activated complex and elimination of water as Frenkel defects. The lower values of Rh and Ir compounds are consistent with the greater volume of these cations and, consequently, the existence of more free space in the lattice to escape the water molecule.

INTRODUCTION

In a very interesting paper, J.E. House [1] proposed a general mechanism for solid state dehydration–anation of coordination compounds in which the generation of a point defect is considered as the formation of the transition state. The two types of point defects considered are analogous to the Schottky or Frenkel types occurring in simple crystals. The dehydration of $[M(H_2O)(NH_3)_5]X_3$ complexes is more consistent, according to House [1], with the formation of a Frenkel type defect and an S_N1 (dissociative) mechanism. Later, LeMay [2] reinterpreted and satisfactorily compared this theory with the literature data. In the same field we have found that the dehydration–anation mechanism of several aquoamine complexes of chro-

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mium(III) and cobalt(III) [3–8] with cyanocomplexes as entering ligands is always consistent with a dissociative mechanism.

If the process takes place by an S_N1 pathway, the rate determining step is the loss of the water from $[M(H_2O)(NH_3)_5]^{3+}$ and the activation energy should be almost invariant with the nature of the anion, provided that the structure of the complexes is very similar. Furthermore, the principal contribution to E_a must be, according to House [1], the Dq factor of M(III) (due to passing from hexacoordination to the intermediate square pyramid). For these reasons, it would be very interesting to compare the kinetic parameters in a series of isostructural complexes with different cations but with the same entering anion, to study the influence of the Dq parameter. In this paper the kinetic parameters for the deaquation–anation of $[M(H_2O)(NH_3)_5]$-$[Co(CN)_6]$ [M = Co, Rh and Ir(III)], and finally the mechanism is discussed, taking into account that for M = Co(III) the kinetics are already widely studied [9–11].

EXPERIMENTAL

Preparation

The $[Co(H_2O)(NH_3)_5][Co(CN)_6]$ was prepared as previously described [12]; $[Rh(H_2O)(NH_3)_5][Co(CN)_6]$ was prepared by mixing an aqueous solution of equimolar quantities of $H_3[Co(CN)_6]$ (obtained by passing the $K_3[Co(CN)_6]$ through a cation exchange resin in its acidic form) and $[Rh(H_2O)(NH_3)_5](ClO_4)_3$ [13,14]. The precipitation is immediate and nearly quantitative. The Ir(III) compound was prepared analogously from $[Ir(H_2O)(NH_3)_5](ClO_4)_3$ [15].

All the elementary analyses (C,N,H and metal) are in complete agreement with the proposed formulae, indicating their anhydrous character. The previous TG measurements also indicate this character. The three compounds are isostructural (X-ray powder diffraction) and with $[Co(NH_3)_6][Co(CN)_6]$ and $[Co(NH_3)_6][Cr(CN)_6]$, the structure is known [16,17].

TG studies

Thermogravimetric studies were carried out on a Perkin-Elmer model TGS-1 system in a nitrogen atmosphere. Non-isothermal measurements were made at a rate of 5° min^{-1}. The amount of sample was 5–7 mg. The kinetic parameters were determined on the basis of the general kinetic relation

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

where $k(T) = k_0 \exp[-E_a/RT]$ (Arrhenius law); k_0 = frequency factor; E_a = activation energy; α = mole fraction. Mathematically, this expression

TABLE 1

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

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

can be converted to

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

The main difficulty in solid kinetics is to find the appropriate expression of $g(\alpha)$ or $f(\alpha)$. In this work, we have used all the principal expressions of $g(\alpha)$ indicated in the literature [18] (Table 1), following the four physical models of solid state chemistry: nucleation, growth, nucleation–growth and diffusion. The more accurate 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. To find the more probable solid state model we have compared this value with the variable values obtained with non-isothermal measurements. In the non-isothermal measurements the expression $g(\alpha)=\int_{T_0}^{T_1}k(T)\mathrm{d}t$ was resolved by the widely employed approximation of Coats and Redfern [19]. 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 water until weight stabilization was obtained. All the calculations were made with the FORTRAN IV program.

RESULTS AND DISCUSSION

The non-isothermal TG curves for the solid phase thermal deaquation of $[M(H_2O)(NH_3)_5][Co(CN)_6]$ are given in Fig. 1. Between 140 and 200°C there is a mass-loss corresponding to a molecular weight decrease of 18 a.m.u. for the Co complex; for the Rh compound the temperature range is

140–190°C and for the Ir compound 150–195°C (in this case the shape of the TG curve is different from the Co and Rh analogues).

In all three cases a new compound was obtained at the end of the curve which corresponds to $[(NH_3)_5M–NC–Co(CN)_5]$ according to spectroscopic measurements [20]. After the water loss, the Co complex immediately begins to decompose, as has already been studied by several authors [9–11]. There is no horizontal region in the TG curve. Instead, the Ir TG run can be prolonged up to 200–220°C without significant decomposition. The Rh compound has an intermediate behaviour (Fig. 1).

The isothermal TG curves at five different temperatures for each product are given in Figs. 2–4.

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

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 account that all the dehydration–anation processes of the aminocomplexes of chromium(III) are never described in terms of the diffusion law we could expect these new compounds to behave according to the growth, nucleation or nucleation–growth laws. Effectively, the E_a, k_0 and r^2 values found with the diffusion model are inconsistent on comparison of the non-isothermal and isothermal measurements. For this reason in Tables 2–4 only the values

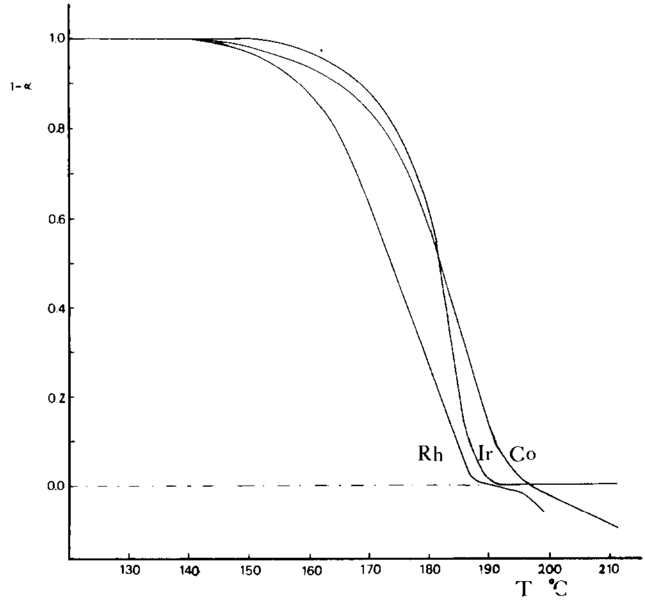
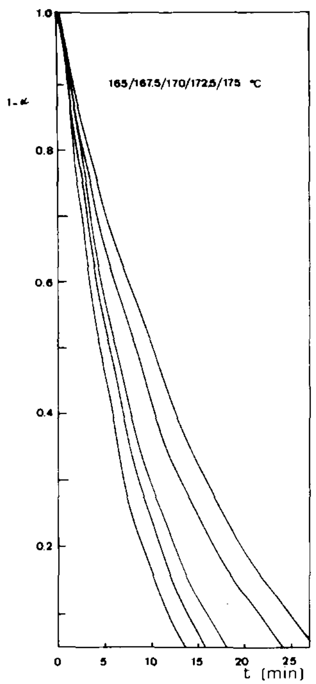


Fig. 1. Non-isothermal TG curves for $[M(H_2O)(NH_3)_5][Co(CN)_6]$ [M = Co(III), Rh(III) and Ir(III)].



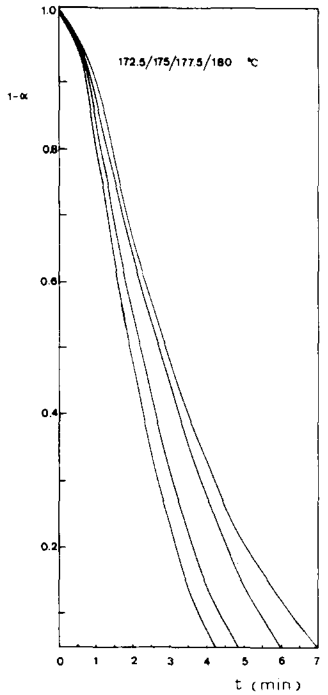


Fig. 2. Isothermal TG curves for $[Co(H_2O)(NH_3)_5][Co(CN)_6]$. The curves are cut at $\alpha = 0.05$ to avoid lengthening the abscissa.

Fig. 3. Isothermal TG curves for $[Rh(H_2O)(NH_3)_5][Co(CN)_6]$. The curves are cut at $\alpha = 0.05$ to avoid lengthening the abscissa.

found for each compound from the growth, nucleation and nucleation–growth models are reported. In order to produce concise information indicating the more prominent features, only the kinetic parameters for a few n values are given in the tables *. It is known from the literature data [21,22] that this apparent order, n, does not have to be an integer but may be also a decimal number.

From Tables 2–4 it is apparent that the E_a and k_0 values can be deduced from the isothermal curves, since the values obtained thus are almost independent of the physical model proposed. The average 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 confirm that the greater E_a is found in the Co complex and the smaller E_a is found in the Ir complex.

In the case of the cobalt(III) complex the activation energy can be compared with previously reported data [9–11]. The value presented here is in good agreement with that of House and Smith [10] (about 140 kJ mol^{-1}) who also employed the isothermal method to obtain this parameter (but without employing the TG technique).

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* The full set of values can be obtained on request from the authors.

TABLE 2

Computational kinetic parameters for $[Co(H_2O)(NH_3)_5][Co(CN)_6]$

	Growth model			Nucleation–growth (Avrami–Erofeev)			Nucleation (Power law)		
	$n = 0$	1/3	2/3	$n = 1$	1.5	2	$n = 0.5$	1	2
Non-isothermal measurements									
E_a (kJ mol^{-1})	150.1	163.8	183.6	199.6	130.6	96.1	307.7	150.1	71.3
x ($k_0 = 10^x$)	16	17	20	22	14	10	34	16	6
r^2	0.9969	0.9982	0.9985	0.9975	0.9974	0.9978	0.9970	0.9969	0.9965
Isothermal measurements									
E_a (kJ mol^{-1})	131.2	128.8	126.3	122.9	126.6	128.6	124.2	131.2	135.4
x ($k_0 = 10^x$)	14	14	13	13	13	14	13	14	14
r^2	0.9919	0.9912	0.9908	0.9911	0.9926	0.9935	0.9857	0.9919	0.9953

TABLE 3

Computational kinetic parameters for $[Rh(H_2O)(NH_3)_5][Co(CN)_6]$

	Growth model			Nucleation–growth (Avrami–Erofeev)			Nucleation (Power law)		
	$n = 0$	1/3	2/3	$n = 1$	1.5	2	$n = 0.5$	1	2
Non-isothermal measurements									
E_a (kJ mol^{-1})	108.6	122.1	142.3	159.1	103.6	75.8	244.5	108.6	50.6
x ($k_0 = 10^x$)	11	13	15	17	11	7	25	11	4
r^2	0.9729	0.9793	0.9858	0.9889	0.9884	0.9878	0.9742	0.9724	0.9683
Isothermal measurements									
E_a (kJ mol^{-1})	115.1	115.8	116.7	117.6	116.6	116.1	116.5	115.1	114.4
x ($k_0 = 10^x$)	12	12	13	13	13	12	12	12	12
r^2	0.9800	0.9792	0.9750	0.9791	0.9861	0.9881	0.9750	0.9800	0.9774

TABLE 4

Computational kinetic parameters for $[Ir(H_2O)(NH_3)_5][Co(CN)_6]$

	Growth model			Nucleation–Growth (Avrami–Erofeev)			Nucleation (Power law)		
	$n = 0$	1/3	2/3	$n = 1$	2	3	$n = 0.5$	1	2
Non-isothermal measurements									
E_a (kJ mol^{-1})	226.2	250.0	285.2	314.3	153.4	99.8	459.9	226.2	109.3
x ($k_0 = 10^x$)	25	27	32	35	16	10	54	25	11
r^2	0.9966	0.9943	0.9892	0.9839	0.9831	0.9823	0.9963	0.9966	0.9963
Isothermal measurements									
E_a (kJ mol^{-1})	89.0	87.7	85.4	83.5	86.8	87.8	85.6	89.0	90.2
x ($k_0 = 10^x$)	9	9	9	9	9	9	9	9	9
r^2	0.9988	0.9962	0.9830	0.9916	0.9927	0.9967	0.9849	0.9988	0.9979

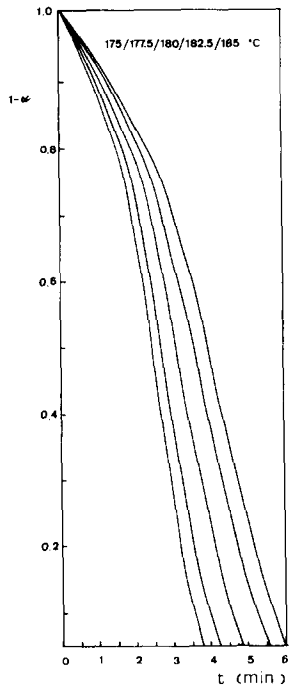

Fig. 4. Isothermal TG curves for $[Ir(H_2O)(NH_3)_5][Co(CN)_6]$. The curves are cut at $\alpha = 0.05$ to avoid lengthening the abscissa.

With regard to the physical model or solid state mechanism, many investigators accept or assume it, i.e., the function g(α) or f(α), 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, also suggested by other authors [23,24], taking into consideration a good value of r^2 and the shape of the isothermal runs [18]. The advantage of this method is the fact that 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 univocal: effectively, in the Co compound there is a good coincidence for E_a, k_0 and r^2 for the Avrami–Erofeev law ($n = 1.5$); but in the Rh compound the same coinci-

TABLE 5

Average kinetic parameters (see text for the model proposed)

Compound	E_a (kJ mol^{-1})	k_0
$[Co(NH_3)_5H_2O][Co(CN)_6]$	129.0 ± 2	1.1×10^{14}
$[Rh(NH_3)_5H_2O][Co(CN)_6]$	110.1 ± 8	1.4×10^{12}
$[Ir(NH_3)_5H_2O][Co(CN)_6]$	93.7 ± 8	1.7×10^{10}

TABLE 6

CFAE (crystal field activation energies) for $[M(H_2O)(NH_3)_5]^{3+}$ cations [M = Co(III), Rh(III), Ir(III)]

Intermediate	CFAE	$[CoH_2O(NH_3)_5]^{3+}$ ($Dq = 25$ kJ mol^{-1})	$[RhH_2O(NH_3)_5]^{3+}$ ($Dq = 38$ kJ mol^{-1})	$[IrH_2O(NH_3)_5]^{3+}$ ($Dq = 45$ kJ mol^{-1})
Dissociative				
Square-based pyramid	4 Dq	100	152	180
Trigonal bipyramid	11.48 Dq	287	436	516
Associative				
Pentagonal bipyramid	8.52 Dq	213	323	383
Octahedral-wedge	3.63 Dq	91	138	163

dence is for the Avrami–Erofeev law ($n = 1.5$), the growth model ($n = 0$) or the power law ($n = 1$) (the last two are mathematically identical). In the Ir compound the best coincidence is for the Avrami law ($n = 3$) or the power law ($n = 2$). Due to the sigmoid shape of the isothermal curves (overall for Rh and Ir complexes), it is probable that the physical model will correspond to the nucleation–growth model, according to the Avrami–Erofeev law [18]. The literature indicates that the sigmoid shape agrees with the Avrami–Erofeev law, where the greater the n value, the greater the sigmoid shape [18]. In this case the more pronounced sigmoid shape is for the Ir compound and corresponds to $\sim n = 3$.

Chemical mechanism

According to the House theory [1], high values of E_a have a better correlation to an S_N2 mechanism, while low values have a better correspondence to an S_N1 mechanism. The compounds studied here have a d^6 configuration. Following the crystal field model of Basolo and Pearson [25] the CFAE (crystal field activation energy) values for each metal are given in Table 6. The values for an S_N2 mechanism are greater than the calculated E_a in all cases except for the Co octahedral-wedge intermediate complex. Furthermore, the heptacoordination in the S_N2 reaction suggests a Schottky defect formation in an ionic crystal (both ions are +3); it would require very high energy ($E_{Sch.} = 0.35$ U, where U is the lattice energy) [26]. Consequently, a value greater than 200–300 kJ mol^{-1} is expected.

It is likely, therefore, that this is an S_N1 (dissociative mechanism) with the formation of a square pyramid activated complex (trigonal bipyramid has too great a CFAE value; Table 6).

According to the Basolo and Pearson theory [25] there are also other unknown factors to add at the 4 Dq (these factors can be either positive or negative).

In the Co case, the value of 130 kJ mol^{-1} is greater than the contribution of Dq (100 kJ mol^{-1}), which seems reasonable. Therefore, the E_a of Rh and Ir complexes would be expected to increase by an order of magnitude. The experimental results are to the contrary, i.e., the lower value is for the Ir complex.

Due to the repetition of the TG measurements, this factor cannot be attributed to the experimental error, but is constitutive of the compound. A reasonable explanation may be due to the compounds isostructurals, with the great volume of the amine cations of Rh and Ir compared with the cobalt. The water loss is the most important step in the S_N1 (dissociative) mechanism. Therefore, the water will be able to escape into the interstitial sites of the lattice when the free space in the net is greater. Therefore, we can expect that the free space will be greater with the more voluminous cation $[Ir(H_2O)(NH_3)_5]^{3+}$ than in the Co cation, with respect to the same anion $[Co(CN)_6]^{3-}$. For this reason, the diffusion of water would be enhanced and the activation energy would be lower than that expected for the CFAE values.

We hope, in the future, to study this apparent anomalism in the series $[M(H_2O)(NH_3)_5]^{3+}$ (M = Co, Rh and Ir) with several other cyanocomplexes as entering anions, to see if effectively the relative size of the ions and the free space is more important than the Dq contribution of the metal ion.

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