

SOLID STATE MECHANISM OF THE THERMAL DEHYDRATION OF $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{X}_3$ ($\text{X} = \text{Cl}^-$, Br^- , I^-)

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ABSTRACT

The solid phase thermal deaquation–anation of $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{X}_3$ ($\text{X} = \text{Cl}^-$, Br^- , I^-) has been investigated by means of isothermal TG measurements applying all the principal $g(\alpha)$ expressions ($0.8 \geq \alpha \geq 0.2$). The values found for the activation energy are low: $\approx 95 \text{ kJ mol}^{-1}$ for the Cl^- compound; $\approx 105 \text{ kJ mol}^{-1}$ for the Br^- compound and $\approx 110 \text{ kJ mol}^{-1}$ for the I^- compound. These data permit the assignment of the deaquation–anation mechanism of the $\text{S}_{\text{N}}1$ dissociative type, involving a square-based pyramid activated complex and elimination of water as Frenkel defects. These values are similar to those reported for the Co(III) and Ir(III) analogues, indicating that the Dq parameter is not the principal contribution to the activation energy of the dehydration–anation process.

INTRODUCTION

Recently [1], we reported the activation parameters for the dehydration–anation processes of $[\text{Ir}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{X}_3$ ($\text{X} = \text{Cl}^-$, Br^- , I^-) and we compared the results with those described in the literature for the Co(III) analogues [2]. On the other hand, in a previous systematic study of the dehydration–anation processes of $[\text{M}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) with several cyanocomplexes as entering anions [3–6], we observed that, although the Dq contribution in the crystal field activation energy (CFAE) is in the order $\text{Ir} > \text{Rh} > \text{Co}$, the E_a values found do not follow this same order but, almost in all cases, the E_a value of the Ir(III) complexes is the lowest, Rh(III) being the intermediate. In order to finish this research, we present here the study of the dehydration–anation processes of $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{X}_3$ ($\text{X} = \text{Cl}^-$, Br^- , I^-) and compare the results with those of the Co(III) and Ir(III) analogues.

There are no previous studies in the literature about the kinetics of these processes. The only data were those reported by Wendlandt and Frank [7] about the dehydration of these salts, without kinetic calculations.

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EXPERIMENTAL

Preparation

The $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{X}_3$ ($\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) compounds were prepared as previously described [8] starting from $[\text{Rh}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ (Johnson-Matthey). All the elementary analyses (C, N, H, X) and electronic and IR spectra were in complete agreement with the proposed formulae. The previous TG measurements indicated an anhydrous character.

TG studies

Thermogravimetric studies were carried out on a Perkin-Elmer (model TGS-2) system in a nitrogen atmosphere. Non-isothermal measurements were made at a rate of 5°C min^{-1} . The amount of sample was 5–7 mg. The kinetic parameters were determined on the basis of the general kinetic relation [9]

$$g(\alpha) = \int_{T_2}^{T_1} K(T) dt$$

where $K(T) = K_0 \exp(-E_a/RT)$ (Arrhenius law), K_0 = frequency factor, E_a = activation energy, α = mole fraction.

In this work, we used all the principal expressions of $g(\alpha)$ indicated in the literature [10] (Table 1), following the four physical models of solid-state chemistry: nucleation, growth, nucleation-growth and diffusion. The most 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 [11]. To find the most probable solid-state model we compared this value with the variable values obtained with non-isothermal measurements,

TABLE 1
Kinetic functions, $g(\alpha)$, used in their integral form

Mechanism	$g(\alpha)$	
<i>Nucleation controlled</i>		
Power law	$\alpha^{1/n}$	R_1
<i>Growth controlled</i>	$[1 - (1 - \alpha)^{1-n}]/(1 - n)$	R_2, R_3
for $n = 1$	$[-\ln(1 - \alpha)]$	F_1
<i>Nucleation-growth controlled</i>		
Avrami-Erofeev	$[-\ln(1 - \alpha)]^{1/n}$	A_2, A_3
<i>Diffusion controlled</i>		
One-dimensional	α^2	D_1
Two-dimensional	$\alpha + (1 - \alpha) \ln(1 - \alpha)$	D_2
Three-dimensional	$[1 - (1 - \alpha)^{1/3}]^2$	D_3
Three-dimensional	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3}$	D_4

and the shape of the isothermal runs. In the non-isothermal measurements the expression of $g(\alpha)$ was resolved by the widely employed approximation of Coats and Redfern [12]. For isothermal analysis the general equation is simply $g(\alpha) = kt$. In this case, an isothermal preheating at a low temperature (50–60°C) was made to eliminate the external water until weight stabilization was obtained. All the calculations were done with a FORTRAN IV program.

RESULTS AND DISCUSSION

The non-isothermal TG curves for the solid-phase thermal deaquation-anation of $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})\text{X}_3]$ are given in Fig. 1. Between 75 and 130°C there was a mass loss corresponding to a molecular weight decrease of 18 a.m.u. for the Cl compound; for the bromo complex the temperature range was 80–130°C and for the iodo complex, 85–135°C.

In all three cases a new compound was obtained at the end of the curve which corresponds to $[\text{Rh}(\text{NH}_3)_5\text{X}]\text{X}_2$, according to spectroscopic measurements. After the water loss, TG runs could be prolonged up to 200°C without significant decomposition.

The isothermal TG curves at five different temperatures for the Br^- product are given in Fig. 2.

In order to calculate the kinetic parameters, all the principal expressions of the solid-state decomposition were used (Table 1), both in isothermal and non-isothermal measurements. The computation for each $g(\alpha)$ and for each

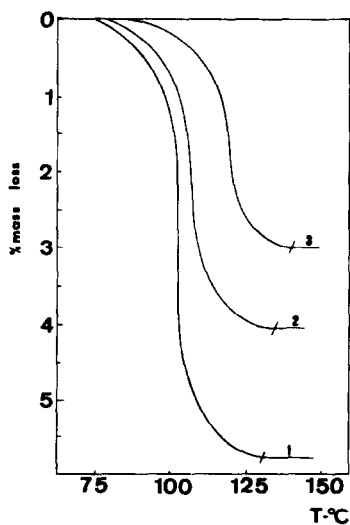


Fig. 1. Non-isothermal TG curves for $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})\text{X}_3]$: (1) $\text{X} = \text{Cl}$; (2) $\text{X} = \text{Br}$; (3) $\text{X} = \text{I}$.

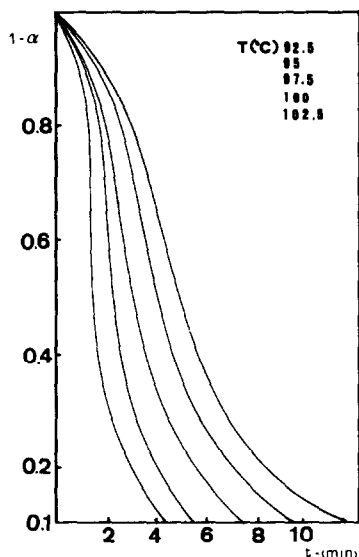


Fig. 2. Isothermal TG curves for $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Br}_3$. The other two are very similar; the curves are cut at $\alpha = 0.1$ to avoid lengthening the abscissa.

n has been carried out with an ad hoc FORTRAN IV program. Taking into account that all the dehydration-anation processes of the amino complexes of the metal(III) were never described in terms of the diffusion law, we should have expected these compounds to have behaved according to growth, nucleation or nucleation-growth. Effectively, the E_a , k_0 and r^2 values found with the diffusion model were inconsistent in comparison with the non-isothermal and isothermal measurements.

The E_a and k_0 values could be deduced from the isothermal curves since the values so obtained were almost independent of the physical model proposed [11]. The average kinetic parameters E_a and k_0 are given in Table 2. Taking into account the possible deviation and error of these values we confirmed that the smaller E_a value was found in the chloro complex and that the E_a values for the bromo and iodo complexes were similar. These values are comparable with those previously reported by us for the same $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ with cyano complexes as entering ligands (Table 3) [3-6].

TABLE 2

Average kinetic parameters

Compound	Solid state mechanism	E_a (kJ mol ⁻¹)	$\ln k_0$
$[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$	Avrami-Erofeev; $n = 2.25$	94.1	25.08
$[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Br}_3$	Avrami-Erofeev; $n = 2.0$	104.3	28.47
$[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{I}_3$	Avrami-Erofeev; $n = 2.25$	110.2	27.98

TABLE 3

 E_a values (in kJ mol^{-1}) for the dehydration-anation processes

	$[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	$[\text{Ir}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	$[\text{Co}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$
Cl^-	94.1 ^a	75.3	89.0
Br^-	104.3 ^a	105.1	84.8
I^-	110.2 ^a	120.7	—
$[\text{Co}(\text{CN})_6]^{3-}$	110.6	93.7	129.0
$[\text{Cr}(\text{CN})_6]^{3-}$	114.5	135.2	—
$[\text{Cr}(\text{CN})_5\text{NO}]^{3-}$	118.6	127.8	104.1
$[\text{Ni}(\text{CN})_4]^{2-}$	105.3	107.7	117.4
$[\text{Pd}(\text{CN})_4]^{2-}$	115.0	118.1	131.0
$[\text{Pt}(\text{CN})_4]^{2-}$	90.2	92.2	66.7

^a This work; the other data are reported in the literature: see text.

With regard to the physical model or solid-state mechanism, i.e., the function $g(\alpha)$ we considered that it may be established by comparison of the dynamic and isothermal conditions, as also suggested by other authors [13], taking into account a good value of r^2 and the shape of the isothermal runs [10]. 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 our case, due to the good comparison between dynamic and isothermal conditions, the value of r^2 and the sigmoidal shape of the isothermal curves, it is probable that the physical model will correspond to the nucleation-growth model, according to the Avrami-Erofeev law [10]. The literature indicates that the sigmoidal shape agrees with the Avrami-Erofeev law, where the greater the n value, the greater the sigmoid shape.

Chemical mechanism

Low values of E_a ($\approx 100 \text{ kJ mol}^{-1}$) have a better correspondence with an $\text{S}_{\text{N}}1$ mechanism while high values of E_a have a better correspondence with an $\text{S}_{\text{N}}2$ mechanism [14,15]. Following the crystal field model of Basolo-Pearson [16], the crystal field activation energy (CFAE) values for Rh(III) complexes, together with those of the Ir(III) and Co(III) analogues, are given in Table 4. The values are greater than the calculated E_a values in all cases. Furthermore, the heptacoordination in the $\text{S}_{\text{N}}2$ reaction suggests a Schottky defect formation in an ionic crystal; it would require very high energy ($E_{\text{Sch.}} = 0.35 U$, where U is the lattice energy [17]). Consequently, a value greater than 200–300 kJ mol^{-1} would be expected.

It is likely, therefore, that this is an $\text{S}_{\text{N}}1$ (dissociative) mechanism with the formation of a square-pyramid activated complex (trigonal bipyramid has too great a CFAE value; Table 4). But supposing an $\text{S}_{\text{N}}1$ mechanism, the E_a

TABLE 4

Crystal field activation energies (CFAE) for $[M(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$, where $M = \text{Co(III)}, \text{Rh(III)}, \text{Ir(III)}$

Intermediate	CFAE	$[\text{CoH}_2\text{O}(\text{NH}_3)_5]^{3+}$ ($Dq = 25 \text{ kJ mol}^{-1}$)	$[\text{RhH}_2\text{O}(\text{NH}_3)_5]^{3+}$ ($Dq = 38 \text{ kJ mol}^{-1}$)	$[\text{IrH}_2\text{O}(\text{NH}_3)_5]^{3+}$ ($Dq = 45 \text{ kJ mol}^{-1}$)
<i>Dissociative</i>				
Square-based				
pyramid	$4 Dq$	100	152	180
Trigonal				
bipyramid	$11.48 Dq$	287	436	516
<i>Associative</i>				
Pentagonal				
bipyramid	$8.52 Dq$	213	323	383
Octahedral				
wedge	$3.63 Dq$	91	138	163

found would be almost independent of the entering anion, as in homogeneous media. Experimentally we found that the E_a values follow the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$ (as in the Ir(III) case, Table 3). A reasonable explanation may be due to the fact that in the solid state we must also take into account other factors, with regard to the solution kinetics. In these "other factors", the free space in the lattice, initially proposed by House [14] and repeatedly confirmed by us [3-6] has a great importance.

Furthermore, if we compare the results for Co(III), Rh(III) and Ir(III) complexes (Table 3) we should notice that while the parameter Dq is in the order $\text{Ir} > \text{Rh} > \text{Co}$, the E_a values do not follow the same order, but in almost all the cases the E_a for Ir(III) complexes is the lowest, Rh(III) being the intermediate value. That is to say, the present work agrees with the previous observed "anomalies" in the Rh(III) and Ir(III) complexes [3-6].

A reasonable explanation for these facts may be due to the ratio of the volume of the cations and anions. 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. Consequently, we should expect that the free space will be greater with the less voluminous Cl^- , compared with the more voluminous $[\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$. In this case, the diffusion of water would be enhanced and the activation energy would be the lowest. However, even with the more voluminous Br^- and I^- , the E_a values found are also smaller than 152 kJ mol^{-1} (CFAE, Table 4). To explain this fact, we suppose that in the House theory [14], applied to the second and third transition series, Rh(III) and Ir(III), the "free space" in the lattice is more important than the Dq contribution of the metal ion. In the future, it will be of interest to study quantitatively, if possible, this contribution which diminishes the expected values of E_a .

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REFERENCES

- 1 J. Ribas and M. Monfort, *Thermochim. Acta*, 91 (1985) 115.
- 2 W.W. Wendlandt and J.L. Bear, *J. Phys. Chem.*, 65 (1961) 1516; W.W. Wendlandt and J.P. Smith, *Nature (London)*, 201 (1964) 291; M. Mori and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, 33 (1960) 841; H.E. Lemay and M.W. Babich, *Thermochim. Acta*, 48 (1981) 147.
- 3 J. Ribas, M. Serra and A. Escuer, *Inorg. Chem.*, 23 (1984) 2236.
- 4 J. Ribas, A. Escuer and M. Monfort, *Thermochim. Acta*, 76 (1984) 201.
- 5 J. Ribas, M. Monfort and X. Solans, *An. Quim.*, 80(B) (1984) 288.
- 6 J. Ribas, A. Escuer and M. Monfort, *Inorg. Chem.*, 24 (1985) 1874.
- 7 W.W. Wendlandt and P.H. Frank, *J. Inorg. Nucl. Chem.*, 26 (1964) 1885.
- 8 T.W. Swaddle and D.R. Stranks, *J. Am. Chem. Soc.*, 94 (1972) 8357.
- 9 D.A. Young, *Decomposition of Solids*, Pergamon Press, Oxford, 1966, Chap. 1; W.E. Garner, *The Chemistry of the Solid State*, Butterworth, London, 1955, Chap. 5.
- 10 C.H. Bamford and C.F.H. Tipper (Eds.), *Comprehensive Chemical Kinetics*, Vol. 22, *Reactions in the Solid State*, Elsevier, Amsterdam, 1980, Chap. 3.
- 11 J.M. Criado, M. Gonzalez, A. Ortega and C. Real, *J. Therm. Anal.*, 29 (1984) 243.
- 12 A.W. Coats and J.P. Redfern, *Nature (London)*, 201 (1964) 68.
- 13 T.B. Chang and N.N. Chandri, *J. Therm. Anal.*, 18 (1980) 247.
- 14 J.E. House, Jr., *Thermochim. Acta*, 38 (1980) 59.
- 15 H.E. LeMay and M.W. Babich, *Thermochim. Acta*, 48 (1981) 147.
- 16 F. Basolo and R.G. Pearson, *Mechanisms of Inorganic Reactions*, 2 edn., Wiley, New York, 1967, p. 67.
- 17 H. Schmalzried, *Solid State Reactions*, Verlag Chemie, Weinheim, 1974, p. 25.