

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

J. RIBAS * and M. MONFORT

Departament de Química Inorgànica, Facultat de Química, Universitat de Barcelona, Diagonal 647, Barcelona (Spain)

(Received 30 March 1985)

ABSTRACT

The solid-phase thermal deaquation–anation of $[\text{Ir}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{X}_3$ ($\text{X} = \text{Cl}^-$, Br^- and I^-) 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 ($0.2 \leq \alpha \leq 0.8$) and by the shape of the isothermal curves. The values found for the activation energy are low ($\sim 75 \text{ kJ mol}^{-1}$ for the Cl^- compound; $\sim 105 \text{ kJ mol}^{-1}$ for the Br^- compound; and $\sim 120 \text{ kJ mol}^{-1}$ 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. The lower value of the Cl^- compound is consistent with the lower volume of this anion regarding the voluminous $[\text{Ir}(\text{H}_2\text{O})(\text{NH}_3)_5]^{3+}$ cation and, consequently, the existence of more free space in the lattice for the water molecule to escape.

INTRODUCTION

In a very interesting paper, House [1] proposed a general mechanism for the 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 $[\text{M}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{X}_3$ ($\text{M} = \text{Co}(\text{III})$, $\text{Cr}(\text{III})$; $\text{X} = \text{Cl}^-$, Br^- , NO_3^-) complexes is more consistent, according to House [1] with the formation of a Frenkel-type defect and an $\text{S}_{\text{N}}1$ (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 chromium(III) and cobalt(III) [3–8] with

* To whom correspondence should be addressed.

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). But, our previous results on amine complexes of Rh(III) and, especially, of Ir(III) are inconsistent with the mean contribution of crystal field activation energy (CFAE) derived from the Dq values [9]. The values found for $[Ir(H_2O)(NH_3)_5][Co(CN)_6]$ and $[Ir(H_2O)(NH_3)_5][CrX(CN)_5]$ ($X = NO, CN$) [9,10] are always very much lower. To see if CFAE is not effectively the principal factor in the Ir(III) compounds, we discuss in this paper the kinetic parameters for the deaquation-anation of $[Ir(H_2O)(NH_3)_5]X_3$ ($X = Cl^-, Br^-, I^-$) and, finally, the mechanism is discussed. In the literature there is a great contribution of information about the Co(III) complexes [11–13] but there is nothing about the Ir(III) complexes.

EXPERIMENTAL

Preparation

The $[Ir(H_2O)(NH_3)_5]X_3$ ($X = Cl^-, Br^-, I^-$) were prepared as previously described [14,15]. All the elementary analyses (C, N, H, X, metal) 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-1) system in a nitrogen atmosphere. Non-isothermal measurements were made at a rate of $5^\circ C \text{ min}^{-1}$. 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 can be converted to

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

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	$(1 - 2/3\alpha) - (1 - \alpha)^{2/3}$

with

$$\int_0^1 d\alpha/f(\alpha) = g(\alpha)$$

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 [16] (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. To find the most probable solid-state model we have compared this value with the variable values obtained with non-isothermal measurements, and the shape of the isothermal runs. In the non-isothermal measurements the expression $g(\alpha) = \int_{T_0}^{T_2} k(T)dt$ were resolved by the widely employed approximation of Coats and Refern [17]. 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 $[\text{Ir}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{X}_3$ are given in Fig. 1. Between 110 and 160°C there is a mass loss corresponding to a molecular weight decrease of 18 a.m.u. for the

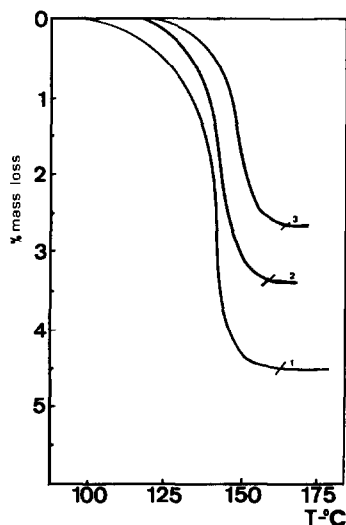


Fig. 1. Non-isothermal TG curves for $[\text{Ir}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{X}_3$. (1) $\text{X} = \text{Cl}$; (2) $\text{X} = \text{Br}$; (3) $\text{X} = \text{I}$.

Cl compound; for the Br complex the temperature range is $115\text{--}165^\circ\text{C}$ and for the I complex, $115\text{--}165^\circ\text{C}$.

In all three cases a new compound was obtained at the end of the curve which corresponds to $[\text{Ir}(\text{X})(\text{NH}_3)_5]\text{X}_2$ according to spectroscopic measurements. After the water loss, TG runs can be prolonged up to $200\text{--}220^\circ\text{C}$ without significant decomposition.

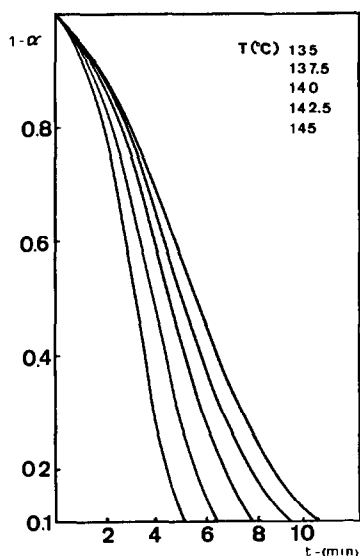


Fig. 2. Isothermal TG curves for $[\text{Ir}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{I}_3$. The other two are very similar; the curves are cut at $\alpha = 0.1$ to avoid lengthening the abscissa.

TABLE 2
Computational kinetic parameters for $[\text{Ir}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{Cl}_3$

	Growth model			Nucleation-growth model (Avrami-Erofeev)			Nucleation model (power law)			
	$n = 0$	0.5	$n = 1$	1.5	2	2.5	3	$n = 0.5$	1	2
<i>Isothermal measurements</i>										
E_a (kJ mol ⁻¹)	73.44	74.83	76.51	75.16	74.53	74.16	73.91	75.52	73.44	72.43
x ($k_0 = 10^x$)	9	10	10	10	10	9	9	9	9	9
r^2	0.9979	0.9999	0.9951	0.9996	1.0000	0.9997	0.9993	0.9987	0.9997	0.9927
<i>Non-isothermal measurements</i>										
E_a (kJ mol ⁻¹)	155.61	183.97	216.61	142.13	104.88	82.54	67.64	318.06	155.61	74.38
x ($k_0 = 10^x$)	19	23	27	18	13	10	8	40	19	9
r^2	0.9978	0.9993	0.9971	0.9970	0.9969	0.9968	0.9967	0.9979	0.9978	0.99975

TABLE 3
Computational kinetic parameters for $[\text{Ir}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{Br}_3$

	Growth model			Nucleation-growth model (Avrami-Erofeev)			Nucleation model (power law)			
	$n = 0$	0.5	$n = 1$	1.5	2	2.5	3	$n = 0.5$	1	2
<i>Isothermal measurements</i>										
E_a (kJ mol^{-1})	103.14	106.27	109.77	106.74	105.25	104.36	103.78	108.52	103.14	100.46
x ($k_0 = 10^x$)	13	14	14	14	13	13	13	14	13	13
r^2	0.9816	0.9871	0.9919	0.9977	0.9952	0.9935	0.9924	0.9906	0.9816	0.9854
<i>Non-isothermal measurements</i>										
E_a (kJ mol^{-1})	172.73	202.85	237.30	155.22	115.22	90.80	74.52	352.32	172.73	82.93
x ($k_0 = 10^x$)	21	25	30	19	14	11	9	44	21	10
r^2	0.9982	0.9977	0.9940	0.9938	0.9936	0.9935	0.9932	0.9982	0.9982	0.9980

TABLE 4
Computational kinetic parameters for $[\text{Ir}(\text{H}_2\text{O})(\text{NH}_3)_5]\text{I}_3$

	Growth model			Nucleation-growth model (Avrami-Erofeev)			Nucleation model (power law)			
	$n = 0$	0.5	$n = 1$	1.5	2	2.5	3	$n = 0.5$	1	2
<i>Isothermal measurements</i>										
E_a (kJ mol ⁻¹)	114.93	119.74	125.75	121.30	120.20	118.20	117.49	121.50	114.93	112.33
x ($k_0 = 10^x$)	14	15	16	15	15	15	15	15	14	14
r^2	0.9974	0.9977	0.9978	0.9982	0.9990	0.9987	0.9982	0.9971	0.9984	0.9989
<i>Non-isothermal measurements</i>										
E_a (kJ mol ⁻¹)	190.13	225.03	265.18	174.47	129.10	101.40	83.75	387.23	190.13	91.59
x ($k_0 = 10^x$)	23	28	33	21	16	12	10	48	23	11
r^2	0.9875	0.9841	0.9873	0.9870	0.9866	0.9863	0.9859	0.9783	0.9775	0.9758

TABLE 5

Average kinetic parameters

Compound	Solid-state mechanism	E_a (kJ mol ⁻¹)	k_0
[Ir(H ₂)(NH ₃) ₅]Cl ₃	Avrami-Erofeev; $n = 2.5$	75 ± 5	0.88 × 10 ⁹
[Ir(H ₂ O)(NH ₃) ₅]Br ₃	Avrami-Erofeev; $n = 2.5$	105 ± 5	0.69 × 10 ¹³
[Ir(H ₂ O)(NH ₃) ₅]I ₃	Avrami-Erofeev; $n = 2.0$	120 ± 5	0.85 × 10 ¹⁵

The isothermal TG curves at five different temperatures for the I⁻ product are given in Fig. 2.

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 metal(III) are never described in terms of the diffusion law, we could expect these 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 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 [18]. It is known from the literature data [19,20] that this apparent order, n , does not have to be an integer but may also be 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 thus obtained 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 smaller E_a value is found in the Cl complex and that the E_a values for the Br and I complexes are similar. These values are comparable with those previously reported by us for [Ir(H₂O)(NH₃)₅][Co(CN)₆], 90 kJ mol⁻¹ [10] and [Ir(H₂O)(NH₃)₅][CrX(CN)₅] (X = CN, NO), 130 kJ mol⁻¹ [9].

With regard to the physical model or solid-state mechanism, i.e., the function $g(\alpha)$ or $f(\alpha)$, many investigators accept or assume it 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 [21], taking into account a good value of r^2 and the shape of the isothermal runs [16]. 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 chloro-compound there is a good coincidence for E_a , k_0 and r^2 for the Avrami–Erofeev law ($n = 2.5$) and for the power law ($n = 2$); in the bromo-compound the same coincidence is found for the Avrami–Erofeev law ($n = 2.5$) or for the power law ($n = 1-2$); in the iodo-complex the best coincidence is for the Avrami–Erofeev law ($n = 2$) or the power law ($n = 1-2$). Due to 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 [16]. The literature indicates that the sigmoidal shape agrees with the Avrami–Erofeev law, where the greater the n value, the greater the sigmoid shape [16].

Chemical mechanism

According to the House theory [1], high values of E_a have a better correspondence 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 [22] the CFAE (crystal field activation energy) values for Ir(III) complexes are given in Table 6. The values are greater than the calculated E_a values in all cases. Furthermore, the heptacoordination in the S_N2 reaction suggests a Schottky defect formation in an ionic crystal; it would require very high energy ($E_{Sch.} = 0.35U$, where U is the lattice energy) [23]. Consequently, a value greater than 200–300 kJ mol⁻¹ is expected.

TABLE 6

CFAE (crystal field activation energy) for $[\text{Ir}(\text{H}_2\text{O})(\text{NH}_3)_5]^{3+}$ cation

Intermediate	CFAE	$[\text{Ir}(\text{H}_2\text{O})(\text{NH}_3)_5]^{3+}$ ($Dq = 45 \text{ kJ mol}^{-1}$)
<i>Dissociative</i> Square-based pyramid	4Dq	180
Trigonal bipyramid	11.48Dq	516
<i>Associative</i> Pentagonal bipyramid	8.52Dq	383
Octahedral- wedge	3.63Dq	163

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 [23] there are also other unknown factors to add at the 4Dq (these factors can be either positive or negative). Effectively, the experimental results are, in all cases, lower than the CFAE.

Due to repetition of the TG measurements, this factor cannot be attributed to the experimental error, but is constitutive of the compounds. A reasonable explanation may be due to the ratio of the volume of the cation and anions. 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 less voluminous anion Cl^- , regarding the voluminous cation $[Ir(H_2O)(NH_3)_5]^{3+}$. In this case, the diffusion of water would be enhanced and the activation energy would be the lowest. However, with the more voluminous anions Br^- and I^- the E_a values found are also smaller than 180 kJ mol^{-1} (CFAE, Table 6). For this fact, we suppose that in the House theory [1], applied to the third transition series, Ir(III), the "free space" in the net is more important than the Dq contribution of the metal ion and, then, the unknown factors must be essentially negative.

ACKNOWLEDGEMENTS

We are grateful for the financial support of C.A.Y.C.I.T. (Spain), Grant 360/81

REFERENCES

- 1 J.E. House, Jr., *Thermochim. Acta*, 38 (1980) 59.
- 2 H.E. LeMay and M.W. Babich, *Thermochim. Acta*, 48 (1981) 147.
- 3 M. Serra, A. Escuer, J. Ribas, M.D. Baró and J. Casabó, *Thermochim. Acta*, 56 (1982) 183.
- 4 M. Corbella, M. Serra, M.L. Martínez and J. Ribas, *Thermochim. Acta*, 57 (1982) 283.
- 5 M. Serra, A. Escuer, J. Ribas and M.D. Baró, *Thermochim. Acta*, 64 (1983) 237.
- 6 J. Ribas, M. Serra and A. Escuer, *Inorg. Chem.*, 23 (1984) 2336.
- 7 M. Monfort, M. Serra, A. Escuer and J. Ribas, *Thermochim. Acta*, 69 (1983) 397.
- 8 M. Corbella, C. Diaz, A. Escuer, A. Seguí and J. Ribas, *Thermochim. Acta*, 74 (1984) 23.
- 9 J. Ribas, M. Monfort and A. Escuer, *Inorg. Chem.*, accepted.
- 10 J. Ribas, A. Escuer and M. Monfort, *Thermochim. Acta*, 76 (1984) 201.
- 11 E.L. Simmons and W.W. Wendlandt, *J. Inorg. Nucl. Chem.*, 33 (1971) 3588.
- 12 J.E. House, Jr. and B.J. Smith, *J. Inorg. Nucl. Chem.*, 39 (1977) 777.
- 13 C.A. Jepsen and J.E. House, Jr., *J. Inorg. Nucl. Chem.*, 43 (1981) 953.

- 14 H.H. Schmidtke, *Inorg. Chem.*, 5 (1966) 1682.
- 15 H.H. Schmidtke, *Inorg. Synth.*, 12 (1970) 243.
- 16 C.H. Bamford and C.F.H. Tipper (Eds.), *Comprehensive Chemical Kinetics*, Vol. 22, *Reactions in the Solid State*, Elsevier, Amsterdam, 1980, Chap. 3.
- 17 A.W. Coats and J.P. Redfern, *Nature (London)*, 201 (1964) 68.
- 18 The full set of values can be obtained on request from the authors.
- 19 D. Blecinc and Z.D. Zivkovic, *Thermochim. Acta*, 60 (1983) 68.
- 20 A.C. Norris, M.I. Pope and M. Selwood, *Thermochim. Acta*, 41 (1980) 357.
- 21 T.B. Chang and M.N. Chandri, *J. Therm. Anal.*, 18 (1980) 247.
- 22 F. Basolo and R.G. Pearson, *Mechanism of Inorganic Reactions*, 2nd edn., Wiley, New York, 1967, p. 67.
- 23 H. Schmalzreid, *Solid State Reaction*, Verlag. Chemie, Weinheim, 1974, p. 25.