

THERMAL STUDIES ON TRIS-CHELATE COMPLEXES OF NICKEL

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A systematic TG/DTG/DTA analysis is reported of anhydrous and heptahydrate forms of tris-phenanthroline and tris-pyridyl complexes of nickel(II), whose kinetic parameters were calculated by five different methods. The dehydration and de-ligation steps are discrete in $\text{Ni}(\text{phen})_3\text{Cl}_2 \cdot 7 \text{H}_2\text{O}$, while those in $\text{Ni}(\text{bipy})_3\text{Cl}_2 \cdot 7 \text{H}_2\text{O}$ are mixed. Partial loss of the ligand is common for both hydrated and anhydrous compounds. In most cases the activation energy E_a calculated from the mechanism-non-invoking equation of Horowitz and Metzger is in good agreement with that found from the mechanism-based relation of Mampel. There is an appreciable variation in magnitude in the results obtained from the different relations for the evaluation of E_a . It is inferred that such kinetic data are of significance in comparisons of the decomposition processes in related systems but not as absolute quantities.

In spite of the large number of studies reported on the thermal analysis of coordination compounds, there are relatively few reports [1–4] on the calculation of the kinetic parameters and their relationship with the nature of the bonding. This may be due primarily to the uncertainties involved in the experimental measurements. Sestak et al. [5] suggested two mathematical approaches, a mechanism-non-invoking one and mechanism-invoking one, for studying the kinetics of decomposition from dynamic TG experiments. Both approaches have previously been applied only to isothermal [6] weight-change studies. Nair and Madhusudanan [4] have recently extended these methods to the deamination of metal complexes. In the present paper we report studies on the kinetics and mechanism of thermal decomposition of anhydrous and heptahydrate nickel complexes: $\text{Ni}(\text{bipy})_3\text{Cl}_2$, $\text{Ni}(\text{phen})_3\text{Cl}_2$, $\text{Ni}(\text{bipy})_3\text{Cl}_2 \cdot 7 \text{H}_2\text{O}$ and $\text{Ni}(\text{phen})_3\text{Cl}_2 \cdot 7 \text{H}_2\text{O}$. Thermal decomposition studies have been reported on similar compounds: $\text{Ni}(\text{bipy})_3\text{Br}_2 \cdot 5\text{H}_2\text{O}$ and $\text{Ni}(\text{bipy})_3\text{Br}_2$ [7]. Calculations of the activation energy, E_r , and the order of the reaction n , are carried out using data from TG, DTG and DTA curves on the basis of the standard treatments reported in the literature.

Experimental

Synthesis of the complexes – Unless otherwise stated, all the reagents used were Fluka products of reagent grade, and were used without further purification.

Tris-bipyridyl- and tris-phenanthroline-nickel (II) chloride heptahydrates were prepared using a reported method [8]. The rosy-pink crystalline products obtained were recrystallized from water.

The anhydrous varieties of the above compounds were prepared using anhydrous starting materials under dry conditions.

The thermal behaviour of these compounds was studied on a MOM derivatograph in an air atmosphere using a platinum crucible at a heating rate of 4°/min. The thermal decomposition products corresponding to the discrete TG plateau regions were isolated. The starting compounds and the isolated decomposition products were characterized via the methods of elemental analysis, electronic and infrared spectra and paramagnetic susceptibility at room temperature.

The evaluation of E_a , A and n was based on a computer program CAL, which incorporates mechanistic and non-mechanistic relations coupled together with least-square fitting of the calculated values. The program has been developed by the authors for use on the ICL-1904 S computer. The DTA and DTG curve resolution was carried out assuming a normal Gaussian shape relation [9, 10].

Results and discussion

The parent complexes and their thermal decomposition products were characterized using physicochemical techniques and the data are presented in Table 1.

Table 1
Chemical analysis and electronic spectral properties

No.	Compound*	% Ni, calc.	Colour	Conductance ⁺ ⁺⁺ ohm ⁻¹ cm ² mole ⁻¹	Band position ⁺⁺ cm ⁻¹
1.	Ni(phen) ₃ Cl ₂ · 7 H ₂ O	7.25 (7.37)	pink	135.0	12 000, 19 000, 29 800
2.	Ni(bipy) ₃ Cl ₂ · 7 H ₂ O	8.0 (8.10)	pink	126.0	12 700, 19 393, 30 303
3.	Ni(phen) ₃ Cl ₂	8.5 (8.76)	green	138.0	10 200, 17 500, 28 000
4.	Ni(bipy) ₃ Cl ₂	9.7 (9.82)	green	154.0	10 800, 18 000, 29 000
5.	Ni(phen) ₂ Cl ₂	11.78 (11.99)	buff	143.0	11 285, 18 700, 29 905
6.	Ni(phen) _{1.6} Cl ₂	13.85 (14.05)	buff	152.0	11 805, 19 200, 30 105

* Analyses of carbon, hydrogen and nitrogen carried out in the microanalytical laboratory, Department of Chemistry, University of Poona, were found to be in agreement with the empirical formulae.

+ Philips GM 4144 bridge; solvent DMF.

++ Beckman DK2 spectrophotometer; solvent ethyl alcohol.

The determination of water of crystallization by the Karl Fischer [11] method confirmed the compositions of the heptahydrates. However, the literature reports [8, 12] indicate varying amounts of water of crystallization. The presence of seven molecules of water was also confirmed from the weight-loss curves. The electronic absorption spectra of the compounds are in conformity with octahedral coordination [13] around the nickel. The solution conductance values indicate a 1 : 2 electrolytic nature, similar to that reported [14].

The TG of $\text{Ni(phen)}_3\text{Cl}_2 \cdot 7 \text{H}_2\text{O}$ shows four steps of decomposition : first, the dehydration step (65° to 165°), second, the loss of one phenanthroline molecule (246° to 350°), while in the third and the fourth steps together 0.4 phenanthroline molecule was lost (410° to 515°); the last two steps were discernible from DTG and were separately treated for the evaluation of the kinetic parameters. The TG of $\text{Ni(bipy)}_3\text{Cl}_2 \cdot 7 \text{H}_2\text{O}$ is very interesting. A six-step decomposition has been observed. The first step obviously represents the loss of seven water molecules (40° to 150°). However, this step is not as discrete as that observed in the TG of the former hydrate, but overlaps with the second step, involving the loss of one bipyridyl molecule (150° to 240°). The next two steps together correspond to the loss of one bipyridyl molecule (250° to 330° , and 337° to 390°). The last two steps account for the loss of only 0.5 bipyridyl molecule (440° to 500° , and 510° to 550°). These observations are similar to those reported by Lee and coworkers [8].

The decomposition behaviour of the heptahydrate was found to be identical to that for the anhydrous phenanthroline compound, except for the loss of water. The loss curve for $\text{Ni(bipy)}_3\text{Cl}_2$ is a little different from that for the heptahydrate. The first step shows the loss of 0.5 bipyridyl molecule (70° to 160°), the second, the loss of 0.75 bipyridyl molecule (210° to 327°), and the next three steps together correspond to the loss of 0.75 bipyridyl molecule (330° to 400° , 420° to 480° , and 495° to 560°). Thus, the compound lost two molecules of bipyridyl up to 560° . The thermal behaviour of the heptahydrate and the anhydrous bipyridyl compound was comparable to that observed for the phenanthroline complexes. The isolation and characterization of all the intermediates in the decomposition, as apparent from the TG curves in Fig. 1, was partially successful. Thus, the intermediates of decomposition of $\text{Ni(bipy)}_3\text{Cl}_2 \cdot 7 \text{H}_2\text{O}$, viz. $\text{Ni(bipy)}_2\text{Cl}_2$, $\text{Ni(bipy)}_{1.33}\text{Cl}_2$ and $\text{Ni(bipy)}_{0.5}\text{Cl}_2$, could be isolated and characterized, while those predicted as $\text{Ni(bipy)}\text{Cl}_2$ and $\text{Ni(bipy)}_{0.75}\text{Cl}_2$ could not. The composition and stereochemistry of these were identical to those reported previously [8], suggesting principally octahedrally coordinated nickel(II). The intermediates isolated from the phen complexes were polynuclear nature (Table I), similarly as observed for the bipy complexes. Only the intermediates $\text{Ni(phen)}_3\text{Cl}_2$, $\text{Ni(phen)}_2\text{Cl}_2$ and $\text{Ni(phen)}_{1.6}\text{Cl}_2$ could be isolated and characterized.

The decomposition process is not similar for the anhydrous and the heptahydrate forms of the bipy complex, whereas in the case of the corresponding phen complexes it is similar except for the loss of water. One of the reasons for this could be the freedom of rotation about the 2-2' bond in bipy. The configuration of phen is comparatively rigid. This could lead to a greater interaction of the associated water

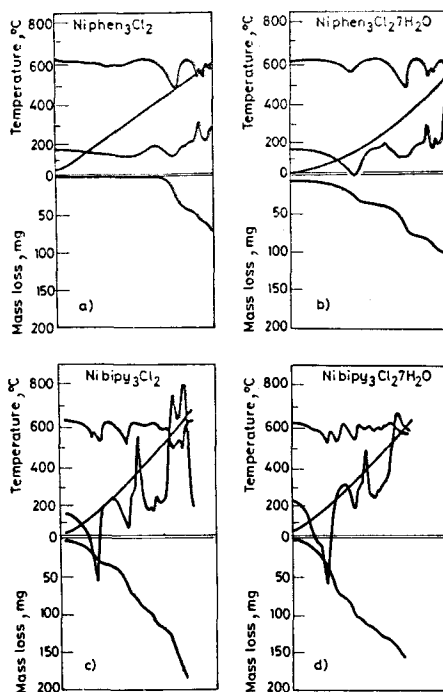


Fig. 1. Thermal curves for anhydrous (a, and c) and heptahydrate (b, and d,) complexes.

molecules in the bipy complex than in the phen complex. Because of the rigidity of phen, the water and the tris-phen complex in the heptahydrate form behave independently of each other, whereas in the bipy they show some kind of cooperative effect. The flexibility in the 2–2' bond in bipy is reported in the literature to be responsible for the higher rates of racemization in its complexes as compared to the rates in the corresponding phen complexes [15]. Similarly, the overall formation constant for the phen complex of Ni(II) is three orders of magnitude higher than that for the bipy complex [15]. This increased stability could be associated with the higher thermal stability of $\text{Ni}(\text{phen})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ over that of $\text{Ni}(\text{bipy})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$. A detailed investigation of the thermodynamics of hydration of the anhydrous complexes may throw some light on this aspect. However, the present investigation is directed mainly towards the kinetics of thermal decomposition of the two related complexes.

The other new observation regarding the thermal stabilities of the hydrated and the anhydrous complexes is worth noting. The heptahydrates of both the complexes are crystalline, are pink in colour, and change reversibly to green-coloured amorphous powders on heating. This behaviour is found to occur in the temperature range 120° to 190° for the phen complex and between 60° and 120° for the bipy complex. The green phen complex was characterized as anhydrous $\text{Ni}(\text{phen})_3\text{Cl}_2$, while the bipy complex was partially anhydrous. When the anhydrous

Table 2
TG data

No.	Compound	Temperature range of decomposition, °C	% loss, (calc.)	Probable composition of	
				expelled group	residue
1.	Ni(phen) ₃ Cl ₂ · 7 H ₂ O	65–165	15.84 (15.83)	7 H ₂ O	Ni(phen) ₃ Cl ₂
		246–350	21.58 (22.62)	phen	Ni(phen) ₂ Cl ₂
		410–470	4.00 (4.52)	0.2 phen	Ni(phen) _{1.8} Cl ₂
		470–515	4.2 (4.52)	0.2 phen	Ni(phen) _{1.6} Cl ₂
2.	Ni(bipy) ₃ Cl ₂ · 7 H ₂ O	40–150	18.0 (17.41)	7 H ₂ O	Ni(bipy) ₃ Cl ₂
		150–240	21.0 (21.53)	bipy	Ni(bipy) ₂ Cl ₂
		250–330	14.8 (15.26)	0.66 bipy	Ni(bipy) _{1.33} Cl ₂
		337–390	6.5 (7.18)	0.33 bipy	Ni(bipy)Cl ₂
		440–500	5.38 (5.26)	0.25 bipy	Ni(bipy) _{0.75} Cl ₂
		510–550	5.38 (5.26)	0.25 bipy	Ni(bipy) _{0.5} Cl ₂

phen complex is heated to above 190° and the partially anhydrous bipy complex to above 120°, the loss of amine starts and the reversibility to the pink form is lost. All these observations suggest that the water of crystallization in the two compounds is responsible for the reversible colour changes. This also implies that the heptahydrate is thermally more stable at room temperature (it conforms to an endothermic process in DTA), and further that as the tris-chelate starts to lose one of the amines the reversibility too is lost. The low temperature of loss for bipy suggests a stronger interaction (through H-bonding) of the water molecules with the complex cation. Table 2 lists the temperature ranges for decomposition, the percentage losses and the probable compositions of the expelled groups and the residues (deduced from the elemental analysis of the isolated residues).

It is evident from the DTA curves that the loss of water and/or the expulsion of the first ligand are endothermic processes, while the subsequent breaking of the residues are all exothermic in nature. The DTA curve shows a clear structural change (235°) just before the commencement of the second step, the loss of phenanthroline from Ni(phen)₃Cl₂ · 7 H₂O. This loss of one phenanthroline molecule could be resolved into two steps on the basis of the unsymmetrical DTA and DTG curves. A similar structural change just before the commencement of the loss of

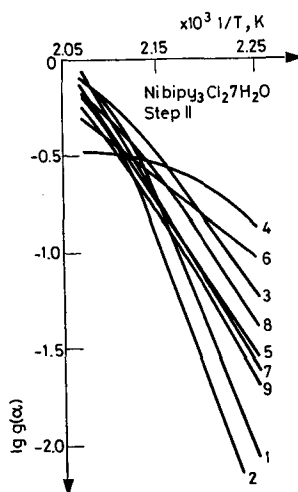


Fig. 2. Satava type plots for $\text{Ni}(\text{bipy})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$, second step. 1. Parabolic, 3. Jander, 4. Ginstling-Brounshtein, 5. Mample, 6. Avrami-I, 7. Avrami-II.

Table 3

Data on activation energy (E_a)

Compound	TG				
	FC		CR		HM
	n	E_a , kJ/mole	n	E_a , kJ/mole	E_a , kJ/mole
$\text{Ni}(\text{phen})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$	1.27	59.3	0.66	69.0	69.0
	1.57	126.0	1.00	87.8	105.0
	1.41	406.0	1.00	345.5	365.0
	1.47	334.0	1.00	334.7	356.0
$\text{Ni}(\text{bipy})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$	1.10	44.3	0.72	42.8	41.9
	1.94	159.0	1.00	142.0	154.5
	1.29	197.0	1.00	164.9	181.0
	1.48	209.0	1.00	181.2	201.3
$\text{Ni}(\text{phen})_3\text{Cl}_2$	1.61	136.0	1.00	125.0	128.0
	1.32	380.0	1.00	359.5	370.0
	1.48	339.0	1.00	320.1	330.0
$\text{Ni}(\text{bipy})_3\text{Cl}_2$	0.62	51.0	0.75	53.0	116.4
	1.40	194.0	1.00	150.3	158.0
	1.35	186.0	1.00	131.8	144.0

FC — Freeman and Carroll, CR — Coats and Redfern, HM — Horowitz and Metzger,

bipyridyl could not be detected in the DTA curve for this heptahydrate. This may be due to the overlapping of the processes of loss of water and loss of the organic ligand. The unsymmetrical DTA and/or DTG curves were resolved by assuming a simple Gaussian shape. The exothermic peaks for the expulsion of the ligands are sometimes so sharp that they could well be misinterpreted as phase transformations. These observations lead to the proposal that the tris chelates are more stable than the bis- and subsequent forms.

The activation energy, E_a , and the order of the reaction, n , were derived using the different relations reported by Arrhenius [16], Borchardt and Daniels [17], Freeman and Carroll [18], Horowitz and Metzger [19] and Coats and Redfern [20]. For elucidation of the correct mechanism, the MacCallum-Tanner [21] equation was used. The α vs. T data thus obtained from the above equation [21] were converted to $\ln g(\alpha)$ vs. T for various models [4, 22]. Values of $\ln g(\alpha)$ were calculated for α above 0.1 only, since the values below this were not reliable. If the correct form of $g(\alpha)$ is chosen, a plot of $\log g(\alpha)$ vs. $1/T$ gives a straight line (Fig. 2). The values of E_a and A have been calculated from the slope and intercept, respectively.

A comparison (Table 3) of E_a for the first step of decomposition of $\text{Ni}(\text{bipy})_3\text{Cl}_2$ with that for the second step of decomposition of the heptahydrate (i. e. the loss of

and order of reaction (n)

DTG				DTA			
A		BD	$n = \frac{A}{BD}$	A		BD	$n = \frac{A}{BD}$
n	E_a , kJ/mole	E_a , kJ/mole		n	E_a , kJ/mole	E_a , kJ/mole	
0.84	69.8	79.4	0.87	0.59	66.4	93.0	0.71
1.29	127.0	116.0	1.09	0.36	58.1	126.0	0.46
1.64	705.0	415.0	1.69	0.95	443.0	454.0	0.97
1.64	359.0	226.0	1.59	1.20	350.0	302.0	1.16
0.39	49.3	145.0	0.34	0.40	47.0	118.5	0.39
0.35	63.7	133.0	0.47	0.81	164.0	180.0	0.91
0.75	207.0	264.0	0.78	1.04	393.0	392.0	1.00
1.08	213.7	205.0	1.04	0.90	207.5	217.5	0.95
1.09	138.0	134.0	1.03	0.77	120.0	154.0	0.78
1.59	680.0	418.0	1.62	1.11	420.0	380.0	1.11
1.20	368.0	300.0	1.22	1.01	343.0	341.0	1.00
0.65	70.0	110.0	0.64	2.20	291.0	137.0	2.13
0.97	150.7	165.0	0.91	0.90	180.0	201.0	0.89
—	—	—	—	0.89	235.0	255.0	0.92

A — Arrhenius, BD — Borchardt and Daniels (assumed $n = 1$).

one bipyridyl group) shows an increase of about three-fold in E_a in the latter case. This increase in magnitude may be attributed to the contribution from the endothermic process associated with the loss of water. This behaviour is similar to the 'intensity stealing mechanism' common in spectral transitions. The overlapping processes of expulsion of water and bipyridyl could be assumed to be contributing together in the overall observed decomposition and thus responsible for the observed enhancement of E_a . A similar observation was not made for the phenanthroline complexes, because the loss step for water is distinctly separate from the loss step for phenanthroline.

It is interesting to note that the ratio of the E_a values calculated from the Arrhenius [16] and the Borchardt and Daniels [17] relations is comparable in magnitude to the order of reaction given by the Arrhenius equation (Table 3). The values of E_a and n have been calculated assuming a Gaussian shape for the curves. The calculations of E_a and n could not be performed from the DTG data for the heptahydrate and anhydrous bipyridyl compounds for the last three steps, owing to the ill-defined envelopes. Since such data do not yield meaningful results, the calculations of E_a , etc. for these three steps were made by assuming them to be one-step processes on the basis of the comparable slopes for these steps in TG loss-curve.

An inspection of Table 3 shows that there is a considerable variation in the magnitudes of E_a calculated via the different models. For a given compound a system-

Table 4
Mechanism of thermal decomposition

Compound	E_a , kJ/mole					Notes
	From mechanism-non-invoking eqn.		From mechanism-based eqn.			
	a	b	c	d	e	
Ni(phen) ₃ Cl ₂ · 7 H ₂ O	59.3	69.0	58.7	47.0	38.2	a(c)
	126.0	105.0	146.0	81.6	52.0	a(c)
	406.0	365.0	360.5	180.2	135.0	b(c)
	334.0	356.0	354.8	—	121.0	b(c)
Ni(bipy) ₃ Cl ₂ · 7 H ₂ O	44.3	41.9	14.9	39.7	17.7	b(c, d)
	159.0	154.5	148.5	77.0	48.0	b(c)
	197.0	181.0	191.5	—	—	a(c)
	209.0	201.3	208.0	190.0	—	a(c)
Ni(phen) ₃ Cl ₂	136.0	128.0	129.0	78.0	50.9	b(c)
	380.0	370.0	359.0	378.2	140.0	b(c)
	339.0	330.0	347.8	—	128.0	a(c)
	51.0	116.4	119.2	59.6	—	b(c)
Ni(bipy) ₃ Cl ₂	194.0	158.0	172.0	83.7	62.0	b(c)
	186.0	144.0	143.2	71.5	—	b(c)

(a) Freeman and Carroll, (b) Horowitz and Metzger, (c) Mampel, (d) Avrami-I, (e) Avrami-II.

atic increase in the magnitude of E_a has been a common observation, irrespective of the relation. Hence to ascertain the most probable value of E_a , for a given weight-loss process, mechanism-based models were employed. The basic treatment of the data was similar to that reported by Nair and Madhusudan [4]; thus, a mechanism-based relation that gives a straight line plot for $\log g(\alpha)$ against $1/T$ has been assumed to be the appropriate process operating for the weight-loss. It may be seen from examination of Tables 3 and 4 that the E_a values derived from the relations based on the TG trace closely agree with those based on mechanistic relations, while the relations based on the DTA and DTG data result in consistently higher values. It could be observed that the processes of de-ligation and dehydration were satisfactorily represented by the Mampel relation. This is similar to that reported [4] on the deamination of metal complexes. The Avrami relation appeared satisfactory only for one step, the dehydration of $\text{Ni}(\text{bipy})_3\text{Cl}_2 \cdot 7 \text{H}_2\text{O}$. Of the three mechanism-non-invoking relations used for processing the TG data, the relation of Horowitz and Metzger [19] seems to give agreeing values in most of the dehydration and de-ligation steps. This relation assumes that the order of the reaction, n , is one. On the other hand, that of Freeman and Carroll [18] indicates that the order, n , is always different from that given by the Horowitz and Metzger relation, even though the magnitudes of E_a are comparable. It may therefore be inferred that the order of the reaction does not provide meaningful information. The activation energy, E_a , however, may be used conveniently for comparison of a given decomposition process for similar compounds. Arnold et al. [23] have recently examined the different important mathematical models for the calculation of kinetic parameters from non-isothermal, quasi-isothermal and quasi-isobaric techniques, and arrived at the conclusion that such data should be accepted with due caution.

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ZUSAMMENFASSUNG — Eine systematische TG/DTG/DTA Analyse für wasserfreie und heptahydrate Formen der Tris-Phenantrolin- und Bipyridylkomplexe von Nickel(II), deren kinetische Parameter durch fünf verschiedene Methoden berechnet wurden, wird beschrieben. Die Dehydratisierung und Abspaltung der Liganden erfolgt im $\text{Ni}(\text{phen})_3\text{Cl}_2 \cdot 7 \text{H}_2\text{O}$, diskret, während sie sich im $\text{Ni}(\text{bipy})_3\text{Cl}_2 \cdot 7 \text{H}_2\text{O}$ überlagern. Ein teilweiser Verlust des Liganden erfolgt sowohl für hydratisierte als auch für wasserfreie Verbindungen. In den meisten Fällen ist die aus dem Mechanismus der Nicht-Invokationsgleichung von Horowitz und Metzger berechnete Aktivierungsenergie E_a in guter Übereinstimmung mit der berechneten aus dem auf dem Mampelschen Zusammenhang beruhenden Mechanismus. Innerhalb der verschiedenen, zur Bewertung von E_a gesuchten Zusammenhänge, besteht eine deutliche Variation in der Größe. Es wird daraus abgeleitet, daß solche kinetische Daten hinsichtlich des Vergleichs der Zersetzungsprozesse verwandter Systeme von Bedeutung, doch nicht als absolute Werte zu betrachten sind.

Резюме — Проведен систематический ТГ/ДТГ/ДТА анализ безводных и семигидратных форм комплексов никеля с фенантролином и дипиридином, для которых кинетические параметры были вычислены пятью различными методами. В случае комплекса $\text{Ni}(\text{фенантр})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ — стадии дегидратации и потери лиганда протекают раздельно, в то время как для комплекса $\text{Ni}(\text{дипир})_3\text{Cl}_2 \cdot 7\text{H}_2\text{O}$ — они смешаны. Общим свойством водных и безводных комплексов является неполная потеря лиганда. В большинстве случаев энергия активации E_a , вычисленная Хоровицем и Метцгером, хорошо согласуется с данными энергии активации, вычисленными из уравнения Мэмпеля. Различные уравнения используемые для оценки E_a , показывают заметные различия значений E_a . Сделано заключение, что такие кинетические данные важны в целях сравнения процессов разложения в ряду родственных систем и не являются абсолютными.