KINETICS OF THE THERMAL DEHYDRATION OF *trans*-FLUOROAQUOBIS(ETHYLENEDIAMINE)CHROMIUM(III) TETRACYANOMETALLATE(II) [METAL(II) = Ni(II), Pd(II) and Pt(II)]

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ABSTRACT

The solid phase thermal deaquation-anation of *trans*-$[CrF(H_2O)(en)_2][M(CN)_4]$ (M = Ni, Pd, Pt; en = ethylenediamine) has been investigated by means of non-isothermal DSC and isothermal and non-isothermal TG measurements. The physical model for these reactions (nucleation, growth, diffusion or intermediates) 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 activation energy are low (~ 130 kJ mol^{-1} for the Ni compound, ~ 140 kJ mol^{-1} for the Pd compound, and ~ 100 kJ mol^{-1} for the Pt compound). These data permit the assignment of the deaquation–anation mechanism of the S_N1 type involving a square-base pyramid activated complex and elimination of water as Frenkel defects.

INTRODUCTION

The solid phase deaquation–anation of aquoamminemetal(III) salts (M(III) = Co(III) or Cr(III)), has been largely studied. For example, the reaction

$$[CoH_2O(NH_3)_5]X_{3(s)} \rightarrow [Co(X)(NH_3)_5]X_{2(s)} + H_2O_{(g)}$$
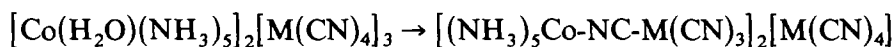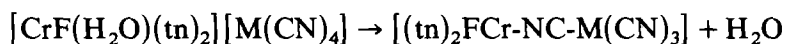
has been studied by several research groups since 1959, notably by Wendlandt and co-workers [1]. The activation energies for these reactions are reported to vary with the anion. Variations in activation parameters with the anion are also reported for the deaquation–anation of $[CrH_2O(NH_3)_5]X_3$ [2] and $[Ru(H_2O)(NH_3)_5]X_3$ [3]. This apparent anion effect was interpreted as an S_N2 (or associative mechanism) ligand exchange between the leaving H_2O and the entering anion, X [2,3].

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However, for the same substance, the activation parameters reported by different research groups are in poor agreement. According to LeMay and Babich [4] 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 that an S_N1 (dissociative) rather than an S_N2 (associative) mechanism is involved in the ligand exchange process.

Following these conclusions, and House [5], an S_N1 process is more consistent with the true activation energies. This S_N1 process is explained in terms of Frenkel defect formation by the elimination of water molecules. Due to the differences in size of the cations and anions, the water molecules may be able to slip into an interstitial position and, thus, escape from the crystal. The activation energy, therefore, must be almost independent of the entering anion.

In the previously reported reactions [6,7]

$$[CrF(H_2O)(tn)_2][M(CN)_4] \rightarrow [(tn)_2FCr\text{-}NC\text{-}M(CN)_3] + H_2O$$

$$[Co(H_2O)(NH_3)_5]_2[M(CN)_4]_3 \rightarrow [(NH_3)_5Co\text{-}NC\text{-}M(CN)_3]_2[M(CN)_4]$$

it was also found that the E_a value is independent of the anion, but only when the structure is the same and there is no distortion in the lattice.

This work comprises thermochemical kinetic studies of the series $[CrF(H_2O)(en)_2][M(CN)_4]$ (en = ethylenediamine; M = Ni, Pd or Pt), which have previously been synthesized and described [8,9]. The kinetic parameters obtained with a series of isothermal TG curves are discussed, which give a value of E_a almost independent of the physical model proposed (nucleation, growth, nucleation–growth or diffusion).

EXPERIMENTAL

TG studies

Thermogravimetric studies were carried out on a Perkin-Elmer TGS-1 system in a nitrogen atmosphere. Non-isothermal measurements were made at a rate of $5°$ min^{-1} with 5–7-mg samples. 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; and α = mole fraction. Mathematically, this expression can be converted to

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

TABLE 1

Kinetic functions, g(α), used in their integral form

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

The main difficulty in solid kinetics is to find the appropriate expressions of g(α) and f(α).

In this work we have used all the principal expressions of g(α) indicated in the literature [16] (Table 1), following the four physical models of solid-state chemistry: nucleation, growth, nucleation–growth and diffusion. The true 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 likely solid-state model this value has been compared with the variable values obtained with non-isothermal measurements. In non-isothermal measurements the expression g(α) = $\int k(T)dt$ was resolved by the widely employed approximation of Coats and Redfern [21]. For isothermal analysis the general equation is simply g(α) = kt. In this case, an isothermal preheating at low temperature (50–60°C) was made to eliminate the external water until the weight remained stable. All the calculations were made with a FORTRAN IV program.

DSC studies

DSC curves were recorded with a Perkin-Elmer DSC-2 with a heating rate of 5° min^{-1} in a nitrogen atmosphere, with 8–10-mg samples.

RESULTS

The reaction enthalpy was calculated by means of dynamic DSC. The curves are given in Fig. 1, and the values obtained are as follows: 129.6 ± 4 kJ mol^{-1} for the Ni compound; 129.6 ± 5 kJ mol^{-1} for the Pd compound; and 146.3 ± 5 kJ mol^{-1} for the Pt compound.

The non-isothermal TG curves for the solid-phase thermal deaquation of *trans*-[CrF(H$_2$O)(en)$_2$][Ni(CN)$_4$] are given in Fig. 2. Between 125 and 230 °C there is a mass loss corresponding to a molecular weight decrease of 18 a.m.u. and a new compound was obtained at the end of the curve which corresponds to [(en)$_2$FCr-NC-Ni(CN)$_3$], according to spectroscopic measurements [8].

The TG curves for the Pd and Pt analogues are very similar, with a slight difference in the starting and final temperatures: 140–230 °C for the Pd compound; and 130–230 °C for the Pt compound.
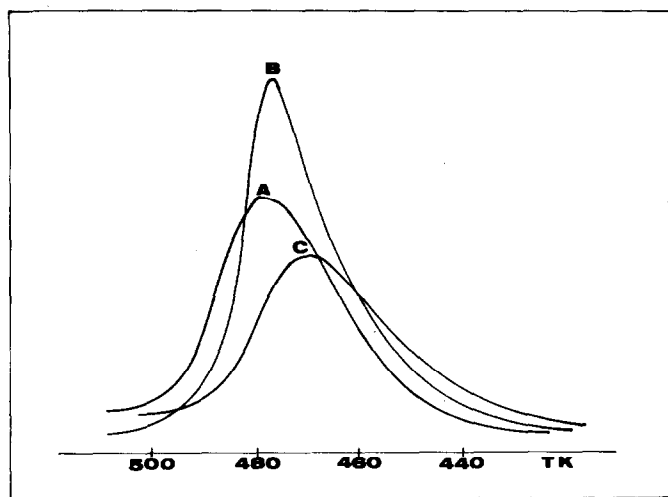

Fig. 1. DSC curves for *trans*-[CrF(H$_2$O)(en)$_2$][M(CN)$_4$] (A) M = Ni(II); (B) M = Pd(II); (C) M = Pt(II).
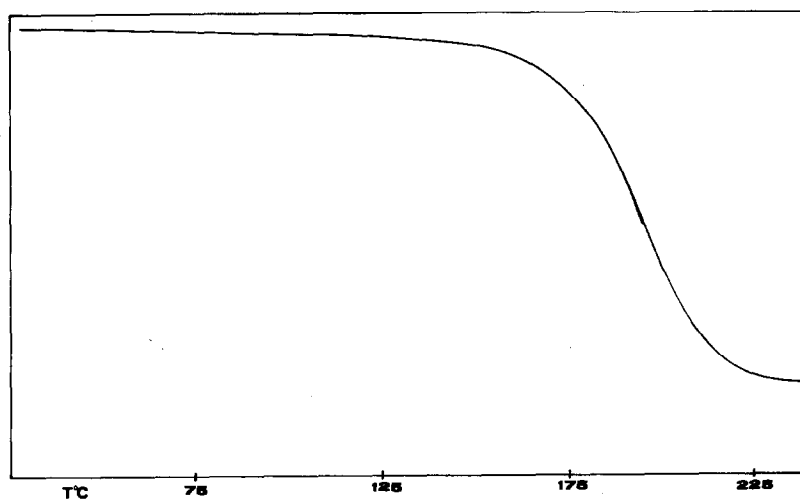

Fig. 2. Non-isothermal TG curve for *trans*-[CrF(H$_2$O)(en)$_2$][Ni(CN)$_4$].

The isothermal TG curves obtained at four different temperatures for each product are given in Figs. 3–5.

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 section).

The results obtained for the new compounds are given in Tables 2–5. The computation for each g(α) 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 aminocomplexes of chromium(III) are never described in terms of the 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 with the diffusion model are inconsistent when comparing the non-isothermal and isothermal measurements. Therefore, only the values found for each compound from the growth, nucleation and nucleation-growth models are reported in Tables 2–4. For brevity, and in order to indicate only the most prominent features, only the kinetic parameters for a few n values are given in these Tables (in fact, these parameters were calculated for more n values). It is known from the literature [10,11] 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 evident that the E_a and k_0 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 true activation energy of the Pt complex (~ 110 kJ mol^{-1}) is somewhat lower than that of the Ni/Pd compounds (~ 130–140 kJ mol^{-1}).

Comparing the activation energy data of other compounds previously reported in the series trans-[CrF(H$_2$O)(en)$_2$]K[CrX(CN)$_5$]H$_2$O (X = NO, CN; $E_a \approx 100$ kJ mol^{-1}) [12] and trans-[CrF(H$_2$O)(en)$_2$]I$_2$ ($E_a \approx 130$ kJ mol^{-1}) [13], it is evident that the Ni/Pd complexes have an activation energy comparable to that of the iodine compound (all are anhydrous).

The values for the Pt and [CrX(CN)$_5$]$^{3-}$ compounds are not comparable because the first is anhydrous and the other two are monohydrates. The great influence of the water of crystallization has been considered in a previous work [13].

The values of k_0 indicate the rigidity of an activated complex. According to Cordes [14] and Shannon [15] the frequency factor may be related to the degrees of freedom of the activated complex and may vary between $\sim 10^5$ and 10^{18}. Small values often indicate a rigid activated complex. The three present cases (Table 5) are intermediate (10^{12} for the Pt compound; 10^{14}–10^{15} for the Ni/Pd compounds).

Many investigators, mainly in non-isothermal TG, assume a certain physical model; i.e., a determined f(α) or g(α). In order to avoid assumptions, the
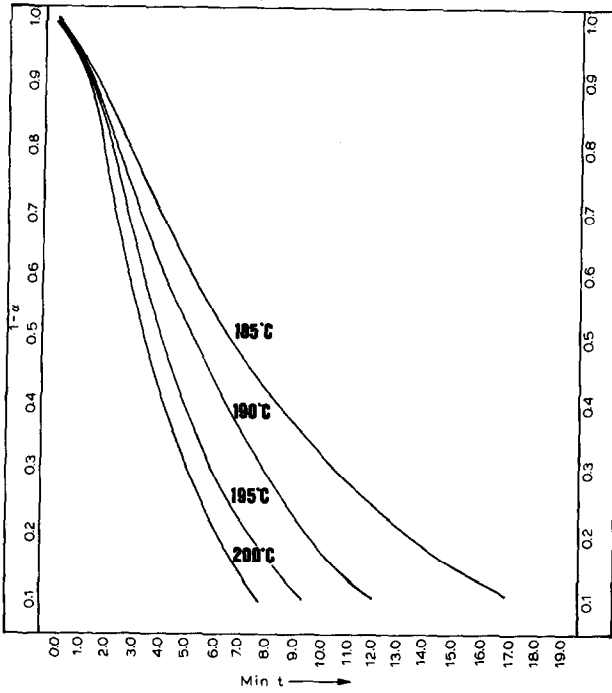
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Fig. 3. Isothermal TG curves for *trans*-[CrF(H$_2$O)(en)$_2$][Ni(CN)$_4$)]. The curves are cut at $\alpha = 0.05-1$ to avoid lengthening the abscissa.
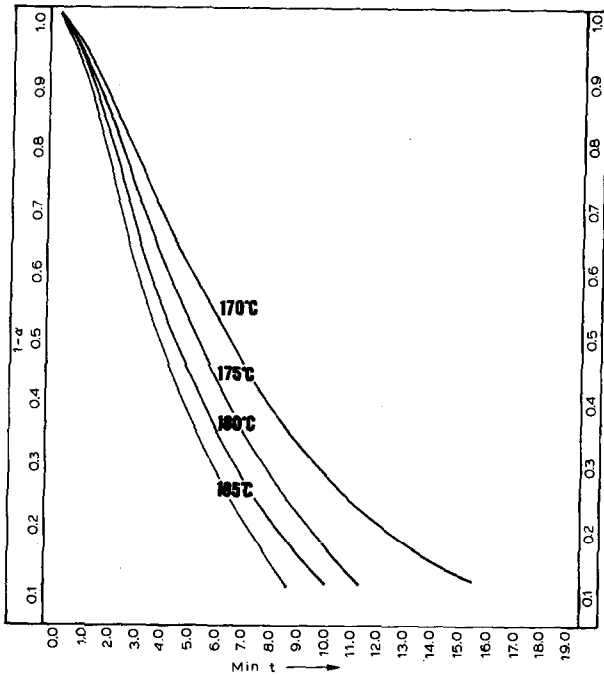

Fig. 4. Isothermal TG curves for *trans*-[CrF(H$_2$O)(en)$_2$][Pd(CN)$_4$]. The curves are cut at $\alpha = 0.05-1$ to avoid lengthening the abscissa.

TABLE 2

Selected values of computational kinetic parameters for trans-[CrF(H$_2$O)(en)$_2$][Ni(CN)$_4$]

	Growth model			Nucleation-growth (Avrami–Erofeev)			Nucleation (power law)		
	n = 0	0.5	0.8	n = 1	1.5	2	n = 0.5	1	2
Dynamic									
E_a (kJ mol^{-1})	97.27	117.43	131.11	140.9	91.32	66.53	202.36	97.27	44.71
$k_0 = 10^x$	9	11	13	14	8	5	20	9	3
r^2	0.9873	0.9961	0.9988	0.9997	0.9996	0.9996	0.9883	0.9873	0.9849
Isothermal									
E_a (kJ mol^{-1})	128.53	128.29	128.25	128.27	128.54	128.76	127.53	128.53	129.42
$k_0 = 10^x$	14	14	14	14	14	14	14	14	14
r^2	0.9996	0.9976	0.9961	0.9950	0.9981	0.9993	0.9930	0.9996	0.9993

TABLE 3

Selected values of computational kinetic parameters for trans-[CrF(H$_2$O)(en)$_2$][Pd(CN)$_4$]

	Growth model			Nucleation-growth (Avrami–Erofeev)			Nucleation (power law)		
	n = 0	0.5	0.8	n = 1	1.5	2	n = 0.5	1	2
Dynamic									
E_a (kJ mol^{-1})	101.95	122.92	137.19	147.44	95.73	69.88	211.58	101.95	47.14
$k_0 = 10^x$	9	12	14	15	9	6	22	9	3
r^2	0.9844	0.9950	0.9983	0.9994	0.9994	0.9994	0.9856	0.9844	0.9817
Isothermal									
E_a (kJ mol^{-1})	138.45	138.48	137.78	137.03	136.53	135.77	142.15	138.45	134.23
$k_0 = 10^x$	16	16	16	16	16	16	16	16	16
r^2	0.9954	0.9982	0.9993	0.9997	0.9984	0.9972	0.9995	0.9954	0.9904

TABLE 4

Selected values of computational kinetic parameters for $trans$-[CrF(H$_2$O)(en)$_2$][Pt(CN)$_4$]

	Growth model			Nucleation-growth (Avrami–Erofeev)			Nucleation (power law)		
	$n = 0$	0.5	0.8	$n = 1$	1.5	2	$n = 0.5$	1	2
Dynamic									
E_a (kJ mol^{-1})	85.18	102.82	114.77	123.32	79.62	57.77	178.12	85.18	38.70
$k_0 = 10^x$	7	9	11	12	7	4	18	7	2
r^2	0.9857	0.9951	0.9982	0.9992	0.9992	0.9991	0.9870	0.9857	0.9826
Isothermal									
E_a (kJ mol^{-1})	101.13	102.25	103.22	104.06	102.80	102.01	102.71	101.13	100.90
$k_0 = 10^x$	10	11	11	12	11	10	11	10	8
r^2	0.9974	0.9969	0.9966	0.9965	0.9966	0.9966	0.9971	0.9974	0.9973

TABLE 5

Average kinetic parameters (see text for the model proposed)

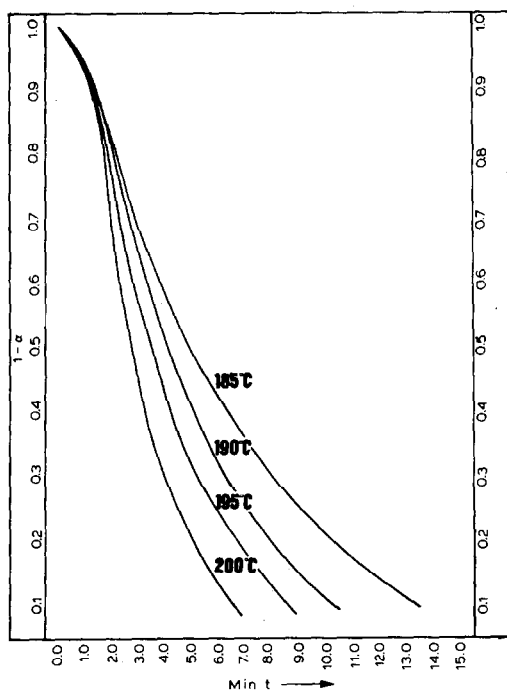| Compound	E_a (kJ mol^{-1})	k_0 (s^{-1})	r^2	$\Delta S^{\#}$ (cal mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
t-[CrFH$_2$O(en)$_2$][Ni(CN)$_4$]	132.1 ± 8.8	0.314×10^{14}	0.9973	1.3 ± 5	124.4	121.7
t-[CrFH$_2$O(en)$_2$][Pd(CN)$_4$]	139.8 ± 7.6	2.264×10^{15}	0.9988	10.1 ± 6	133.6	114.8
t-[CrFH$_2$O(en)$_2$][Pt(CN)$_4$]	111.0 ± 10	0.103×10^{12}	0.9976	−11.5 ± 4	98.7	121.2

Fig. 5. Isothermal TG curves for *trans*-$[CrF(H_2O)(en)_2][Pt(CN)_4]$. The curves are cut at $\alpha = 0.05 - 1$ to avoid lengthening the abscissa.

solid-state mechanism may be established by comparing the dynamic and isothermal conditions, using an accurate value of r^2, and taking into consideration the shape of the TG isothermal runs, as suggested by other authors [16,17]. The advantage of this method is 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, there is a good agreement for the Avrami law with $n \approx 1.2$; for the growth model with $n = 0.5-0.8$; or for the power-law with $n = 0.8-1.0$ (in all cases the Avrami model has a better regression coefficient, r^2; Tables 2-4).

Due to the sigmoid shape of the isothermal curves in the three compounds the physical model will probably correspond 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 shape, the greater the n value [16]. In the present case the three compounds do not show a very pronounced sigmoid shape and correspond to $n \approx 1.0-1.5$.

DISCUSSION

House [5] 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 E_a values correspond better to an S_N2 mechanism, while low values correspond better to S_N1. In the present case (d^3), in an S_N2 reaction, the formation of a seven-bond activated complex (pentagonal bipyramid) based on a crystal field model requires 4.26 Dq [18], Dq being ~ 25 kJ mol^{-1} for the aquo-amine complexes of chromium(III), which alone would be ~ 105 kJ mol^{-1}.

If the activated complex was an octahedral-wedge, the energy required would be only 1.8 Dq (nearly 50 kJ mol^{-1}). However, in an S_N2 reaction, the heptacoordination requires a Schottky defect formation in an ionic crystal, which, in turn, requires a high amount of energy ($E_{Sch.} = 0.35$ U, U = lattice energy) [19]. Consequently, a value of > 130 kJ mol^{-1} would be found.

It is likely, therefore, that this is S_N1 (dissociative mechanism) with the formation of a square pyramid activated complex, requiring only 2 Dq [18] ($E_a \approx 50$ kJ mol^{-1}); a trigonal bipyramid activated complex would require 5.7 Dq, i.e., 145 kJ mol^{-1}, greater than the E_a value found. Consequently, the transition state is determined by the water loss and a non-ionic Frenkel defect formation.

The difference between the activation energy of trans-[CrF(H_2O)(tn)_2] [M(CN)_4] (tn = 1,3-diaminopropane; M = Ni, Pd, Pt; ~ 100 kJ mol^{-1} in all three cases [6]) and the three complexes studied here also gives proof of the dissociative mechanism, the water loss being the more important step of the reaction. The water can escape into the interstitial sites of the lattice when the free space in the lattice is increased. Evidently, the free space is expected to be greater with the more voluminous tn ligand than with the en ligand.

It is not clear why the energy value is lower in the Pt case than in the Ni/Pd compounds; taking into account the similar size of the $[M(CN)_4]^{2-}$ anions (M = Ni, Pd, Pt) and the isostructuralism of the three salts, the E_a value should be of the same order of magnitude. In the previously reported series, $[CoH_2O(NH_3)_5]_2[M(CN)_4]_3$ (M = Ni, Pd, Pt) [7], the marked difference between Pt and Ni/Pd compounds (about a half in the Pt case) was interpreted in terms of a strong Pt–Pt interaction in the crystal lattice, causing distortion and thus allowing water molecules to escape easily from the crystal structure.

For this reason, although these Pt–Pt interactions are not found spectrally in the mixed complex salts, but only in the dinuclear complexes obtained after heating [8,20], it is suggested that the interaction begins during heating and causes a lower value of the activation energy in the Pt salt.

Furthermore, the entropy of activation calculated from the expression

$$\ln kh/K_B T = \Delta S^\# / R - \Delta H^\# / RT$$

(where k = rate constant; and K_B = Boltzmann constant) may also indicate differences between Ni/Pd and Pt compounds (Table 5). According to

House [5] the entropy effect may also be explained by the relative sizes (in this case the relative packing) of the ions and the free volume: where there is more space between the cations and anions (as is supposed in the Pt compound, due to the Pt–Pt association) the water molecules may be able to slip into an interstitial position causing little or no lattice distortion. Therefore, the activation entropy may be small, or slightly negative. Where there is less space between the ions (as can be supposed in the Ni–Pd compounds) the water molecules can occupy an interstitial position only with considerable lattice expansion, so that the activation entropy is positive.

Although this entropy reasoning of House is speculative, and not supported by any facts, we believe that it gives an intuitive explanation of the process.

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