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THERMOCHEMICAL PARAMETERS OF THE THERMAL DEHYDRATION OF *TRANS*-[CrF(H_2O)(1,3-DIAMINOPROPANE)$_2$][M(CN)$_4$] (M = Pd, Pt)

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ABSTRACT

The solid phase thermal de-aquation of *trans*-[CrF(H_2O)(tmd)$_2$][M(CN)$_4$] (M = Pd, Pt) (tmd = 1,3-diaminopropane) has been investigated by means of DSC and TG measurements. The enthalpy of reaction has been determined and the activation energy has been found by non-isothermal and isothermal kinetic studies. The values found for the activation energy are low and similar to those reported for the analogous compound *trans*-[CrF(H_2O)(tmd)$_2$][Ni(CN)$_4$] (about 120 kJ mole^{-1}) and permit the assignment of a de-aquation–anation mechanism of the S_N1 type, involving penta-coordinated activated species and elimination of water as Frenkel defects.

INTRODUCTION

The solid-phase de-aquation–anation of aquopentaamminecobalt(III) salts

$$[Co(H_2O)(NH_3)_5]X_{3(s)} \rightarrow [CoX(NH_3)_5]X_{2(s)} + H_2O_{(g)}$$

has been studied by several research groups since 1959, notably by Wendlandt and co-workers [1–4] and Mori and co-workers [5–7]. The activation energies for these reactions are reported to vary with the anion. The variation in activation parameters with the anion are also reported for the de-aquation–anation of [Cr(H_2O)(NH_3)$_5$]X_3 [8,9] and [Ru(H_2O)(NH_3)$_5$]X_3 [10]. This apparent anion effect signifies an S_N2 (or associative mechanism) ligand exchange between the leaving H_2O and the entering anion, X.

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Recently, House [11] has proposed a defect diffusion model to explain it. However, for the same substance, the activation parameters reported by different research groups are in poor agreement [12]. According to Lemay [12], this is due to the fact that the experimental conditions have not been specified or controlled. Accordingly, it is of the utmost importance to use the same conditions and the same equations to be able to compare the data obtained. Thus, as Lemay points out [12], when procedural variables are held constant, activation parameters for different salts agree within experimental error. This could mean [11,12] that an S_N1 (dissociative) mechanism is involved in the ligand exchange process.

In a previous report [13] on the de-aquation–anation of *trans* [CrF(H_2O)(tmd)$_2$][Ni(CN)$_4$] the following values of E_a were found: 120 kJ mole^{-1} (dynamic TG), 115 kJ mole^{-1} (isothermal TG) and 120 kJ mole^{-1} (DSC). The agreement among the values indicates that: (a) the equations applied in TG and DSC approach the likely mechanisms of the solid-state process; (b) the relatively low values suggest, according to House [11], a de-aquation–anation mechanism of the S_N1 (dissociative) type with formation of Frenkel defects; that is, the transition state is determined by the water loss and the formation of a non-ionic Frenkel defect.

The previous report [13] finished with the statement, "This implies no variation of E_a regarding similar anions, in which, a priori, the mechanisms would be identical. In the near future we intend to verify this with the [Pd(CN)$_4$]$^{2-}$ and [Pt(CN)$_4$]$^{2-}$ ions".

The present paper gives a report of a kinetic investigation of the de-aquation–anation of *trans*-[CrF(H_2O)(tmd)$_2$][M(CN)$_4$] (M = Pd, Pt) with a comparison with the results obtained for the analogous compound containing [Ni(CN)$_4$]$^{2-}$ [13]. This study involves both isothermal and non-isothermal experiments, using TG and DSC techniques. Great care was exercised to ensure that the experimental conditions were as uniform as possible.

EXPERIMENTAL

Preparation of trans-*[CrF(H_2O)(tmd)$_2$][M(CN)$_4$] (M = Pd, Pt)*

The salts may be prepared in the anhydrous or hydrated form [14]. To obtain the anhydrous form, 1 g of K_2[Pd(CN)$_4$] [15] or K_2[Pt(CN)$_4$] (Johnson and Matthey) was dissolved in 10 ml of water and the solution passed through Amberlite IR 20 A in the H^+ form. One gram of finely-ground *trans*-[CrF(H_2O)(tmd)$_2$](ClO$_4$)$_2$ [16,17] was added with constant stirring to the ice-cold solution. The pink solid which formed was filtered, washed with ethanol and ether, and dried.

TG studies

Thermogravimetric studies were carried out on a Perkin-Elmer model TGS-1 system at a rate of 10° min^{-1} in a nitrogen atmosphere. The amount of sample used was 6–7 mg. The activation energy was determined on the basis of the general kinetic relation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(T)\,\mathrm{f}(x)$$

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

The main difficulty in solid kinetics is to find the approximate expression of $\mathrm{f}(x)$. The more widely used equations have been described by Criado et al. [18]. Practically all the authors take $\mathrm{f}(x) = (1-x)^n$ in the deaquation–anation reactions (n being the so-called order of reaction). We shall assume it to be valid in the kinetic study of our products; thus, the activation energy and reaction order may be obtained by non-isothermal and isothermal methods, respectively. For the non-isothermal method, we shall use the widely employed approximation of Coats and Redfern [19]. For the isothermal analysis the general equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(T)\,\mathrm{f}(x)$$

with $\mathrm{f}(x) = (1-x)^n$, becomes $1-(1-x)^{1-n} = k(1-n)t$, except when $n = 1$, in which case it is equivalent to $\ln(1-x) = -kt$.

All the calculations were done with a FORTRAN IV ad hoc program, taking n from 0 to 1, at 0.1 intervals.

DSC studies

The DSC studies were carried out using a DSC-2 Perkin-Elmer differential scanning calorimeter under the same conditions as the TG studies. Since the best linear fit was obtained for $n = 0.0$ in both cases (see Results and Discussion), all the calculations were done applying the equation of Thomas and Clarke [20] which holds only when the order of reaction is zero. In or Sn were used as standards to calculate the reaction enthalpies.

RESULTS AND DISCUSSION

The TG curve for the solid-phase thermal de-aquation of *trans*-$[\mathrm{CrF(H_2O)(tmd)_2}][\mathrm{M(CN)_4}]$ are given in Figs. 1 and 2 for M = Pd and Pt, respectively. A mass loss corresponding to a molecular weight decrease of 18 a.m.u. occurred at ca. 418 K in both cases and a dark pink compound was obtained at the end of the first peak, which corresponds to *trans*-$[\mathrm{(tmd)_2FCr}$-

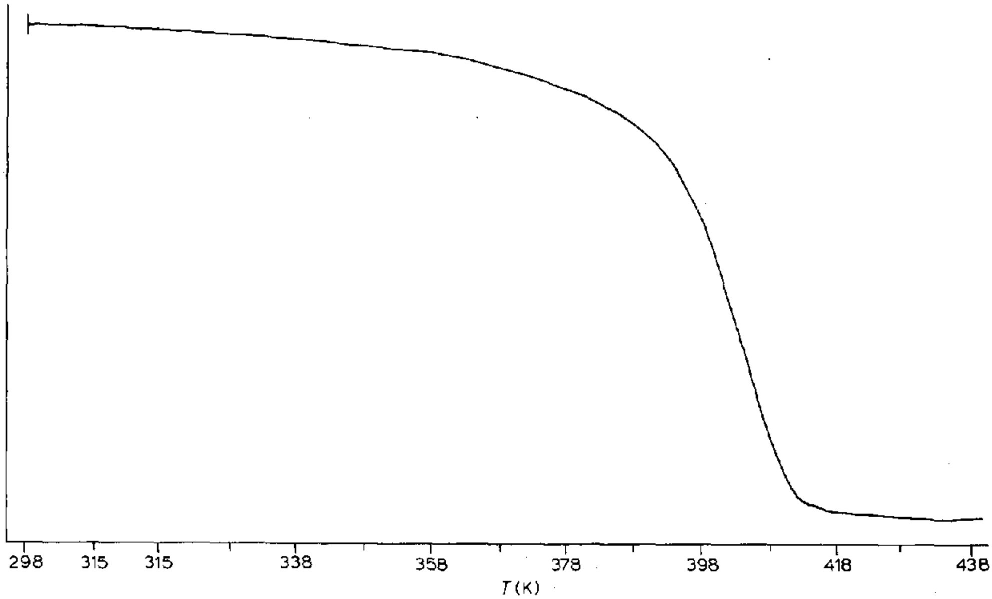

Fig. 1. TG curve of *trans*-$[CrF(H_2O)(tmd)_2][Pd(CN)_4]$.

$NC\text{-}M(CN)_3]$ (M = Pd, Pt), compounds which have previously been synthesized by the authors [14]. In order to characterize the TG curves obtained, the reaction order, n, activation energy, E_a, and the pre-exponential factor, k_0, have been obtained using the Coats and Redfern equations [19]. The curves were analysed from $n = 0$ to $n = 1$ at 0.1 intervals. The best correla-

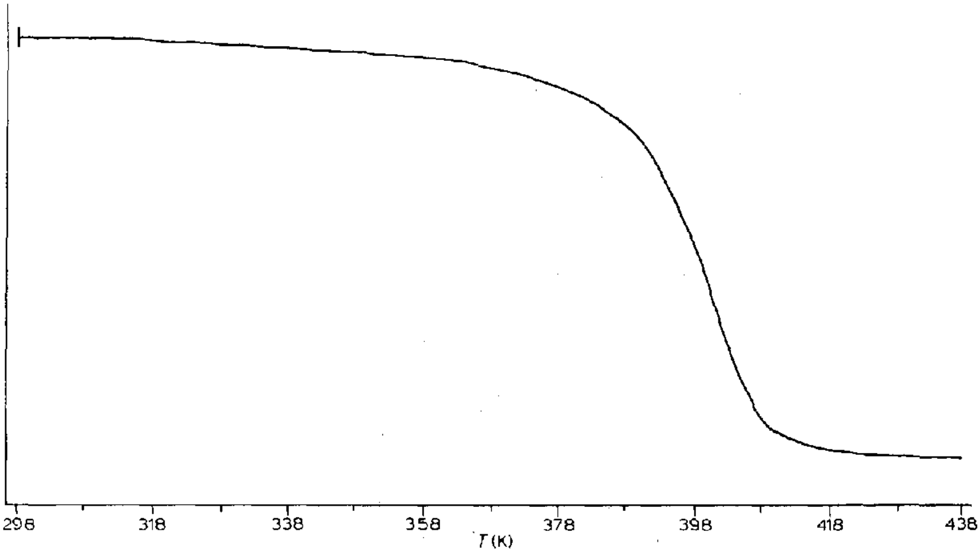

Fig. 2. TG curve of *trans*-$[CrF(H_2O)(tmd)_2][Pt(CN)_4]$.

tion coefficient was found for $n = 0.0$ (0.9986 for Pd and 0.9990 for Pt). The same result ($n = 0.0$) was also found for the analogous compound containing $[Ni(CN)_4]^{2-}$ [13]. A value of $n = 0.0$ corresponds to a uniform reaction occurring over the surface with no contraction of the reaction interface area [21]. There is no considerable variation in the E_a values when a given order is assumed. Thus, when $n = 0.0$, the mean activation energy is 118.0 ± 5 kJ mole^{-1} for the $Pd(CN)_4^{2-}$ compound and 120.2 ± 6 kJ mole^{-1} for the $Pt(CN)_4^{2-}$ compound. As to the frequency factor, we found $k_0 = 5 \times 10^{12}$ for the Pd compound and 2×10^{13} for the Pt compound. According to Cordes [22] and Shannon [23], the frequency factor is related to the degrees of freedom of the activated complex and may vary between 10^5 and 10^{18}. Small values often indicate a rigid activated complex without degrees of freedom and high values indicate a flexible activated complex. The present cases [as in the case of the $Ni(CN)_4^{2-}$ derivative with $k_0 = 10^{12}$] are intermediate.

The values of E_a have been analyzed with isothermal methods and compared with the dynamic values in order to show the validity of the kinetic law. A number of experiments were performed at several constant temperatures, not much higher than those at which the non-isothermal curves showed the first deflection from the base line. The curves obtained are given in Figs. 3 and 4 for Pd and Pt compounds, respectively. It must be pointed out that these curves are not real but modified with an ad hoc FORTRAN IV program so that all of them appear at the same scale for easier comparison. Besides, in order not to widen the curves unnecessarily, the program represents $(1 - x)$ vs. time from $(1 - x) = 0$ to 0.95 and not to 1, which is what is obtained in the real TG curve.

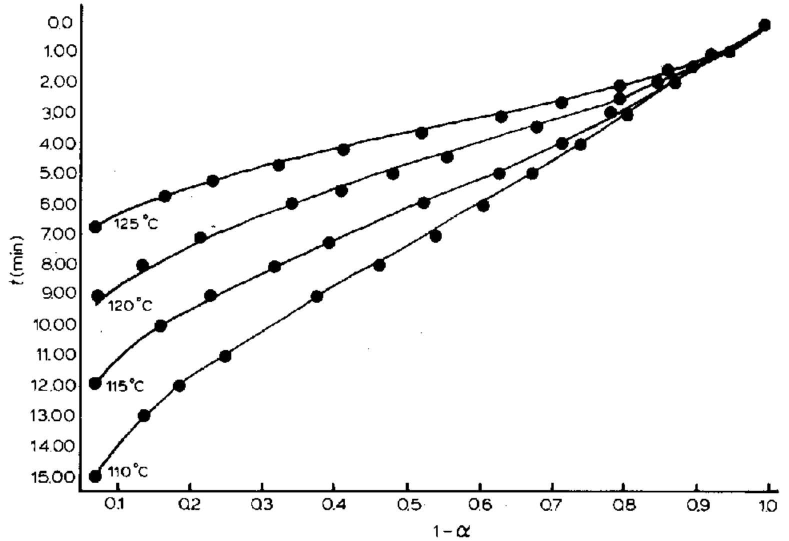

Fig. 3. TG isothermal curves of *trans*-$[CrF(H_2O)(tmd)_2][Pd(CN)_4]$.

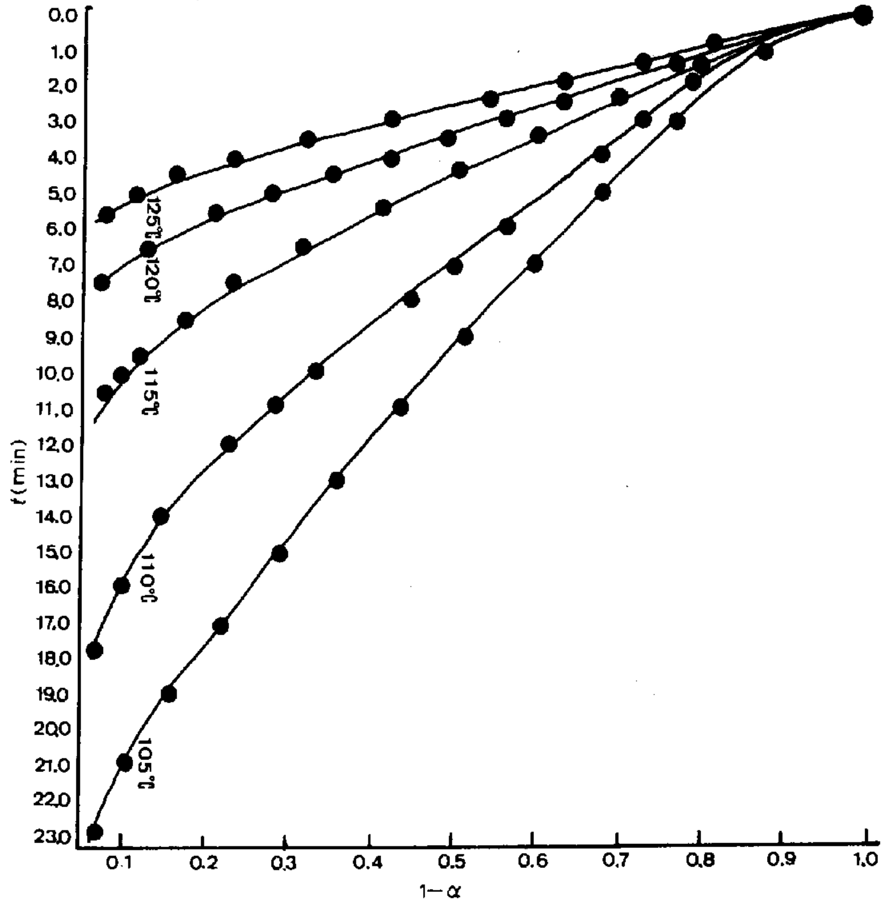

Fig. 4. TG isothermal curves of *trans*-[CrF(H_2O)(tmd)$_2$][Pt(CN)$_4$].

Since the reaction order found is 0.0, the applied equation, $1-(1-x)^{1-n} = k(1-n)t$, becomes $x = kt$. Therefore, if $n = 0.0$, a plot of x vs. t must be a straight line going through the origin and with slope k. Figures 5 and 6 show that the lines are straight in the interval $x = 0.2$–0.8 which is where the calculations are carried out. The straight lines, by extrapolation, meet at a point located nearly in the origin (ideal case). The rate constants were determined at different temperatures from the slopes of these lines and then the activation energy (E_a) was calculated using the Arrhenius equation. The values of E_a are 102.8 ± 8 kJ mole^{-1} for the Pd compound and 104 ± 6 kJ mole^{-1} for the Pt compound.

The kinetic de-aquation parameters derived from the non-isothermal studies, although somewhat high are consistent with those obtained from isothermal methods.

Analysis of the DSC curves (Fig. 7) in the de-aquation region, using the

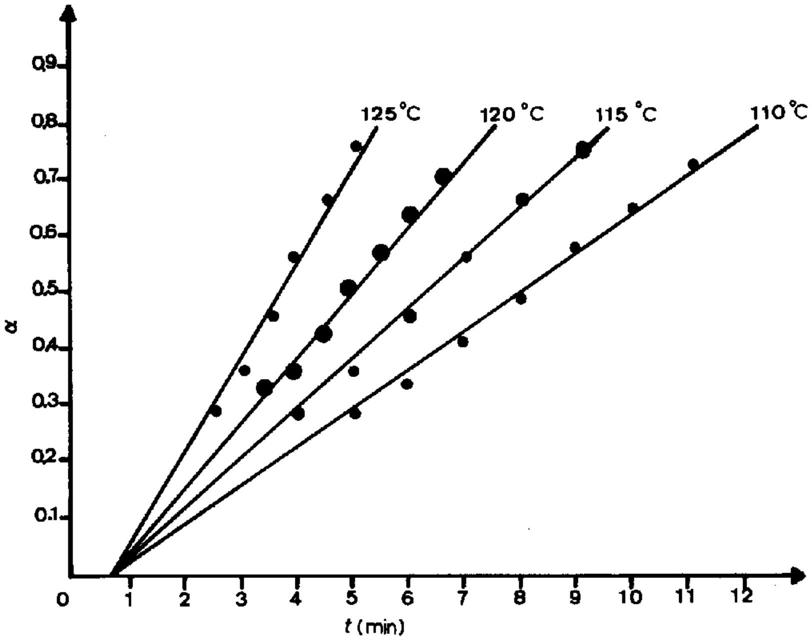

Fig. 5. $\alpha(x)$ vs. t of TG isothermal curves of *trans*-$[CrF(H_2O)(tmd)_2][Pd(CN)_4]$.

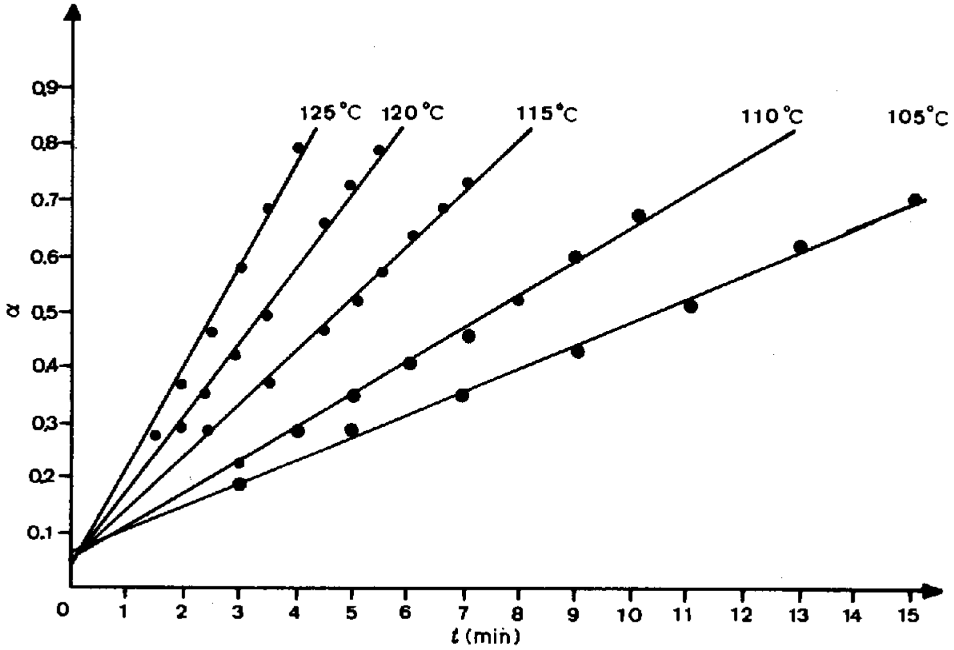

Fig. 6. $\alpha(x)$ vs. t of TG isothermal curves of *trans*-$[CrF(H_2O)(tmd)_2][Pt(CN)_4]$.

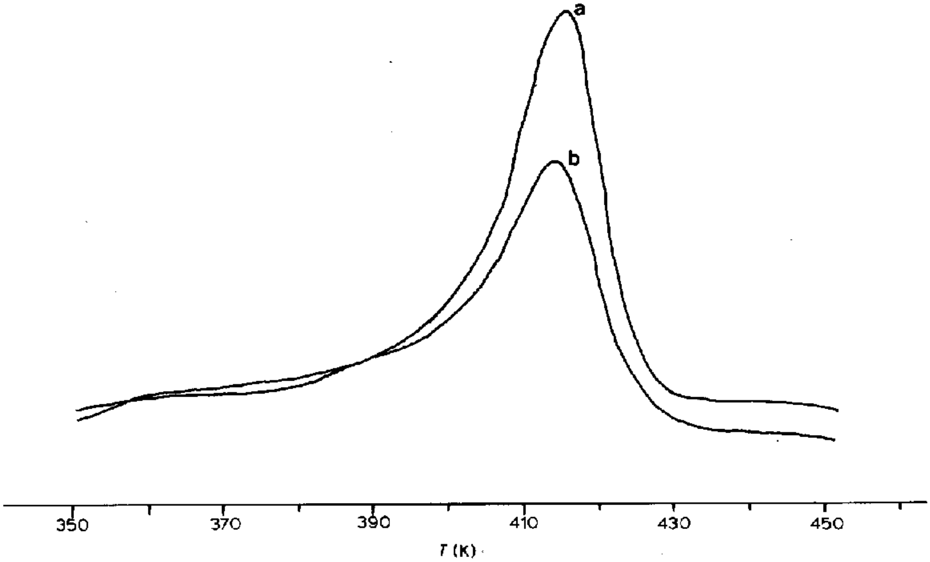

Fig. 7. DSC curves of (a) *trans*-[$CrF(H_2O)(tmd)_2$][$Pt(CN)_4$] and (b) *trans*-[$CrF(H_2O)$-($tmd)_2$][$Pd(CN)_4$].

approximate (but valid for $n = 0$) method of Thomas and Clarke, give activation energies of 125.0 ± 5 and 130.5 ± 5 kJ mole^{-1}, respectively, agreeing with the values obtained from TG (notably in the non-isothermal method).

The enthalpy changes for these processes, using In or Sn as standards are 76 ± 4 and 78 ± 4 kJ mole^{-1}, respectively.

Mechanism

House has recently proposed [11] several mechanisms for the de-aquation–anation reactions of solid complexes based on the formation of Schottky or Frenkel defects. According to this author, two factors are important: (a) the value of the energy of activation, and (b) the variation of this energy with respect to the outer anating anion. As to the values of E_a, House indicates that a high value of E_a corresponds better to an S_N2 mechanism while a low value means an S_N1 mechanism. For an S_N2 mechanism, the contribution of the ligand field in the formation of the hepta-coordinated activated complex can vary from 4.26 to 1.8 *Dq* for a pentagonal bipyramid or octahedral wedge, respectively [24]. Since for our Cr(III) complexes *Dq* is about 2000 cm^{-1} (25 kJ mole^{-1}), the ligand field contribution will be 106.5 kJ mole^{-1} or 45 kJ mole^{-1}, respectively. Furthermore, other contributions must be added as indicated by Basolo [24]. On the other hand, an associative mechanism involves the formation of an ionic Schottky defect which demands a larger amount of energy (about 0.4 U_0; $U_0 =$ lattice energy) [25]. The sum of all these contributions gives values higher than those found by the authors for both complexes (about 120 kJ mole^{-1}). On the other hand, a dissociative mechanism (formation of a non-ionic Frenkel defect by loss of a water molecule which goes to the interstices in the crystal lattice and is eventually eliminated), would imply a very low contribution to E_a. The ligand field contribution for the two most likely geometries for a penta-coordinated activated complex are 2 Dq (50 kJ mole^{-1}, square pyramid) and 5.7 Dq (145 kJ mole^{-1}, trigonal bipyramid) [24]. By comparison with the experimental values an activated complex with a trigonal bipyramid geometry may be eliminated, leaving an associative (S_N1) mechanism involving a square-pyramid activated complex.

This assertion is confirmed on comparing the values found for different anions of similar geometry $[M(CN)_4]^{2-}$ [M = Ni, Pd, Pt]. In this case and within the experimental error and the reliability of the applied equations, the three complexes give E_a values of about 110–120 kJ mole^{-1}. The equality of values indicates that the mechanism is of a dissociative (S_N1) type.

Of course, the bond energy involved in the anation process should be taken into account if the anions are totally different. In other words, it would be interesting to study the process with anions other than $[M(CN)_4]^{2-}$, such as sulphate, dithionate or simply halides. The authors believe this is a suggestive field for future research.

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