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# $\Delta H$ AND ACTIVATION ENERGY OF DEHYDRATION–ANATION PROCESSES CALCULATED FROM DYNAMIC TG AND DTA

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## ABSTRACT

Thermodynamic ($\Delta H$) and kinetic parameters (activation energy, $E$) for the dehydration–anation processes of the doubly complexed salts $[M(H_2O)(NH_3)_5][Co(CN)_6]$ (M = Co,Rh,Ir(III)), $[Co(H_2O)(NH_3)_5]_2[M'(CN)_4]_3$ and $[CrF(H_2O)(en)_2][M'(CN)_4]$ (M′ = Ni, Pd, Pt(II); en = ethylenediamine) have been determined. The $\Delta H$ values have been measured by DTA. The $E$ values have been obtained by DTA and dynamic TG using the same equation.

One can observe an increase in $E$ and a decrease in $\Delta H$ for the Pt compounds that exhibit a Pt–Pt interaction.

## INTRODUCTION

In recent years [1] we have worked on factors affecting the kinetics of the dehydration–anation processes of aquo-complexes, like $[M(H_2O)(NH_3)_5]X_3$ and *trans*-$[CrF(H_2O)(aa)_2]X_2$ (M = Cr(III), Co(III), Rh(III), Ir(III); aa = ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane; X = anions like halides or cyanoderivatives of Ni(II), Pd(II), Pt(II), Co(III), etc.). For example, one of these reactions is [2]

$$[M(H_2O)(NH_3)_5][Co(CN)_6] \rightarrow [(NH_3)_5M\text{–}NC\text{–}Co(CN)_5] + H_2O$$

The systematic study of these reactions has shown, according to literature data [3], that the true activation parameters must be calculated by isothermal TG methods, with supporting dynamic procedures to discover the physical

TABLE 1

$\Delta H$ values (with corresponding standard deviation) and activation energy values for the two techniques (DTA and TG). $\Delta T$ corresponds to the range $\alpha = 0.2$ to $\alpha = 0.8$ in DTA and TG runs

| Complex | $\Delta H$ (kJ mol$^{-1}$) | $E$ (kJ mol$^{-1}$) | | $\Delta T$ (K) | |
|---|---|---|---|---|---|
| | | DTA | TG | DTA | TG |
| $[Co(H_2O)(NH_3)_5][Co(CN)_6]$ | $45 \pm 3$ | 199 | 271 | 457–469 | 446–461 |
| $[Ir(H_2O)(NH_3)_5][Co(CN)_6]$ | $48 \pm 1$ | 314 | 340 | 460–470 | 448–459 |
| $[Rh(H_2O)(NH_3)_5][Co(CN)_6]$ | $51 \pm 3$ | 159 | 284 | 445–456 | 438–455 |
| $[Co(H_2O)(NH_3)_5]_2[Pt(CN)_4]_3$ | $78 \pm 1$ | 141 | 186 | 384–397 | 372–389 |
| $[Co(H_2O)(NH_3)_5]_2[Pd(CN)_4]_3$ | $45 \pm 1$ | 156 | 250 | 380–389 | 379–394 |
| $[Co(H_2O)(NH_3)_5]_2[Ni(CN)_4]_3$ | $54 \pm 7$ | 123 | – | – | 389–407 |
| $[CrF(H_2O)(en)_2][Pd(CN)_4]$ | $58 \pm 2$ | 140 | 284 | 460–472 | 452–473 |
| $[CrF(H_2O)(en)_2][Ni(CN)_4]$ | $54 \pm 5$ | 132 | 249 | 461–475 | 459–484 |
| $[CrF(H_2O)(en)_2][Pt(CN)_4]$ | $59 \pm 7$ | 111 | 188 | 458–475 | 455–482 |

processes occurring at the reaction interface (nucleation, growth, nucleation–growth, diffusion). When we compared our results with those in the literature [4], we found that the principal problem is the great variety of working conditions (heating rate, grain size, sample weight, etc.) which considerably affects the results. However, a more significant problem is the apparent impossibility of comparing results obtained from different techniques, mainly when results concern only one or two compounds.

In this communication, for nine complexes (listed in Table 1) previously studied by us with isothermal TG [1d,1g], we present a comparison of the kinetic values obtained with DTA and dynamic TG, and the change of enthalpy values determined by DTA. Although these techniques are different, and DTA is subject to criticism for kinetic determinations [5], we have tried to keep the experimental conditions as similar as possible, taking into consideration the limitations of the techniques.

## EXPERIMENTAL

### *Preparation of compounds*

The nine complexes were prepared as previously described [1d,1g].

### *Calorimetric studies*

DTA studies were carried out in two different furnaces with a great thermal resistance between crucibles [6]. We have worked with a static air atmosphere in furnace A (chromel–alumel thermocouples, sensibility 4.7 mV

$W^{-1}$ at 400 K), where systematic measurements have been made. The $\Delta T$ signal amplification was $5 \times 10^3$ and the sample mass was approximately 20 mg. In furnace B (Pt–Pt/10%Rh thermocouples, sensibility 0.5 mV $W^{-1}$ at 400 K) used as a test in order to compare $\Delta H$ results, a dynamic nitrogen atmosphere was used, $\Delta T$ signal amplification was $2.5 \times 10^4$ and sample mass was about 10 mg. Typical heating rates in both furnaces were 5 K $\text{min}^{-1}$. CSi has been used as a reference substance. We have used open Al cylindrical crucibles ($m = 35$ mg). $KNO_3$ transition (II → I) and Sn melting were used for temperature and energy calibration [7].

We have obtained the differential signal or thermogram in numerical form (sampling period = 2 s). A minimum of five measurements in furnace A and two in furnace B were carried out for each complex.

### *Thermogravimetric studies*

The TG runs were performed on a Perkin-Elmer model TGS-1 in a nitrogen atmosphere. Non-isothermal measurements were made at a heating rate of 5 K $\text{min}^{-1}$. The amount of sample was 5–7 mg. We have obtained the TG curves on a graphic recorder.

## DETERMINATION OF KINETIC PARAMETERS

Activation energies were determined on the basis of the general kinetic relation

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{1}$$

where $k(T) = k_0 \exp(-E/RT)$ (Arrhenius law); $k_0$ = frequency factor; $E$ = activation energy; $\alpha$ = mole fraction (range used = 0.2–0.8). Mathematically, this expression can be converted to

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha'}{f(\alpha')} = \int_{T_0}^{T} \frac{k(T')}{\beta} dT' \tag{2}$$

The main difficulty in solid-state kinetics is to find the appropriate expression of $g(\alpha)$ or $f(\alpha)$. In this work we solved eqn. (2) by the widely employed approximation of Coats and Redfern [8] with $f(\alpha) = (1 - \alpha)^n$, applied to the complexes studied, for different values of $n$.

## RESULTS AND DISCUSSION

The DTA thermograms of the nine complexes are given in Fig. 1. In Fig. 2 we show an example of the dynamic TG curves obtained. From these runs

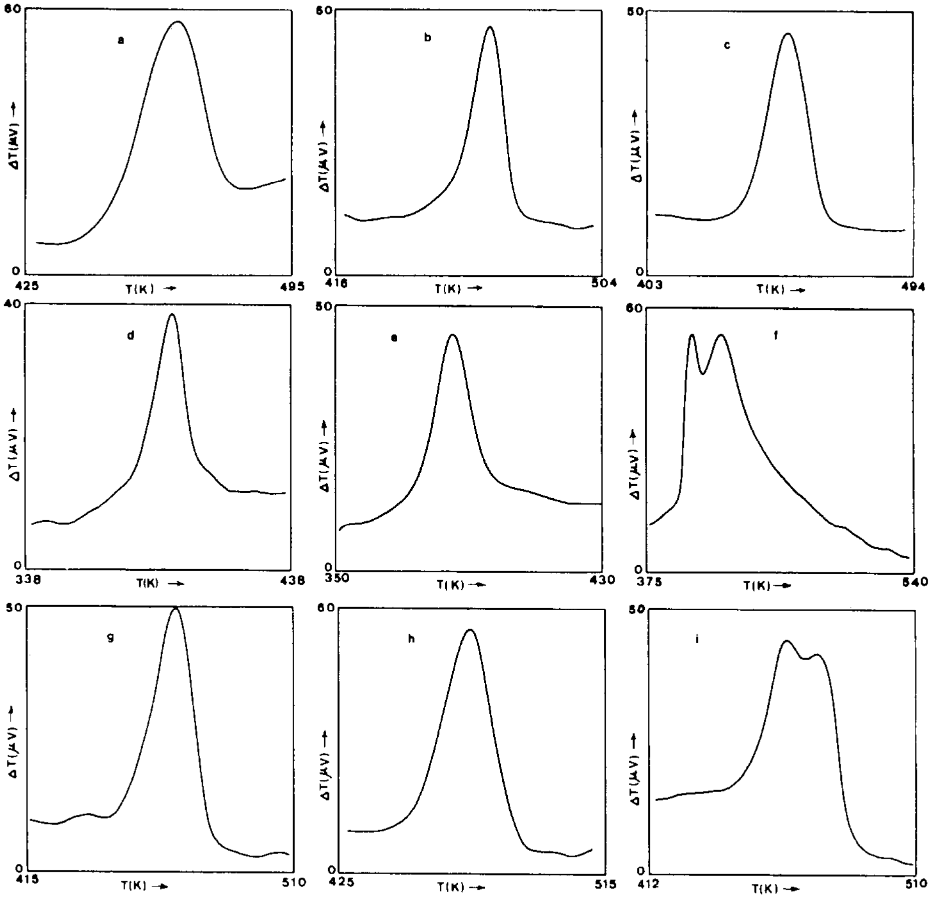

Fig. 1. DTA thermograms for the complexes studied. $[M(H_2O)(NH_3)_5][Co(CN)_6]$: (a) M = Co, (b) M = Ir, (c) M = Rh. $[Co(H_2O)(NH_3)_5]_2[M'(CN)_4]_3$: (d) M′ = Pt, (e) M′ = Pd, (f) M′ = Ni. $[CrF(H_2O(en)_2][M'(CN)_4]$: (g) M′ = Pd, (h) M′ = Ni, (i) M′ = Pt.

we have calculated the enthalpy change for the dehydration–anation reaction and the activation energy of the same process (Table 1). In Table 1 we only give the values corresponding to $n = 1$, using the growth (Coats and Redfern) or nucleation–growth (Avrami) models (mathematically equal for $n = 1$). We have chosen this case for two reasons:

(a) The Avrami equation for $n = 1$, or 1.5 is the more adequate to fit the real process in these dehydration–anation reactions, as has been shown in other works on these and other analogous compounds, from isothermal measurements [1].

(b) The variation of the kinetic parameters (not the absolute values) is always similar to those found with Avrami model *.

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* All these values are obtainable on request to the authors.

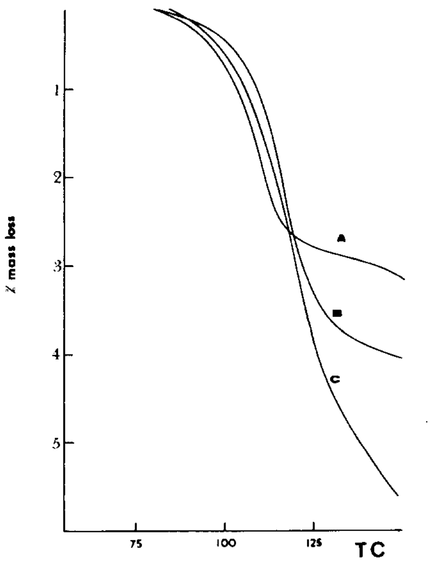

Fig. 2. Dynamic TG runs for $[Co(H_2O)(NH_3)_5]_2[M'(CN)_4]_3$. (A) M' = Pt, (B) M' = Pd, (C) M' = Ni.

With the DTA technique, $\Delta H$ values are in good agreement for the two furnaces used (differences less than 7%). It is necessary to point out that the $[M(H_2O)(NH_3)_5]X_3$ complexes, apart from the dehydration–anation process studied here, present at higher temperatures one peak corresponding to the decomposition processes which can overlap the main peak. This is the case for $[Co(H_2O)(NH_3)_5][Ni(CN)_4]_3$ (Figs. 1f and 2C). Using the inverse filtering technique we have deconvoluted this thermogram in order to separate both processes. For this reason, the estimated value of $\Delta H$ is given with a wide error margin and the activation energy is not determined by DTA. The $\Delta H$ values listed in Table 1 are very similar for all the series, and only compounds with Pt are more differentiated. In the dehydration processes, the ease of loss of water depends basically on the cation/anion size relationship of the compound. The possibility for water molecules to enter interstitial positions is regulated by the free space existing in the lattice. So, apart from the true kinetic parameters, which have to be calculated by isothermal TG methods, the activation energy values for the Pt compounds which exhibit Pt–Pt interactions are comparatively lower by both techniques. Correspondingly, Pt compounds also present higher $\Delta H$ values, notably so for $[Co(H_2O)(NH_3)_5][Pt(CN)_4]_3$. For the other complexes, the $\Delta H$ values are similar and correspond to the similarity of the process analysed.

Comparing the thermogravimetric and calorimetric methods, we have found that the activation energy values are always greater with the DTA technique. The significant differences between TG and DTA can be attributed to the direct measure of the ordinates in the TG runs and, instead, to the calculated ratio partial area/total area of the peak, for each temperature in DTA. This fact may be relevant as is indicated in Table 1: the corresponding temperatures at $\alpha = 0.2$ and $\alpha = 0.8$ agree between the two techniques, although to determine the kinetic values we include the effect of the shape of the curve.

The variety of results gives, in some way, a level of acceptability. For example, in the literature there is very good agreement in the kinetic parameters compared with results obtained by the DSC technique for $[CoH_2O(NH_3)_5][Co(CN)_6]$ [1d,9–11]. Instead, regarding the enthalpy changes, the value obtained by Simmons and Wendlandt (49 kJ $mol^{-1}$) is in the moiety of the interval of variation found with DTA and DSC [1d], whereas those in refs. 10 and 11 are not in agreement.

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