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SOLID STATE KINETIC PARAMETERS OF THE FIRST DECOMPOSITION OF POTASSIUM DICHLOROTETRACYANOPLATINATE(IV), DIBROMOTETRACYANOPLATINATE(IV) AND DIIODOTETRACYANOPLATINATE(IV)

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ABSTRACT

The first solid state reductive elimination of $K_2[Pt(CN)_4X_2]$ (X = Cl, Br, I) has been studied by thermogravimetric measurements both in non-isothermal and isothermal conditions. The first decomposition reaction produces $\frac{1}{2}(CN)_2$ for one mole of the chloro and bromo compound and I_2 for one mole of the iodo compound. The activation energies obtained for these processes are: 240 kJ mol^{-1}, 245 kJ mol^{-1} and 100 kJ mol^{-1} respectively. These values are found by the isothermal method and agree with with those obtained by the non-isothermal method. In both cases, all the expressions for the solid state model (growth, nucleation, nucleation-growth and diffusion) were applied. The real solid-state model (nucleation-growth according to the Avrami–Erofeev law) is obtained by comparison between the non-isothermal and isothermal methods and by studying the shape of the isothermal runs.

INTRODUCTION

In the last few years we have studied the kinetics and mechanism of solid state dehydration–anation processes such as

$$[M(NH_3)_5(H_2O)]_2[M'(CN)_4]_3 \rightarrow [(NH_3)_5M\text{-}NC\text{-}M'(CN)_3]_2[M'(CN)_4]$$
$$[M = Co(III), Rh(III), Ir(III); M' = Ni(II), Pd(II), Pt(II)]$$

and similar systems [1]. As a result we have demonstrated, after the theory expounded by LeMay and Babich [2] and House [3] that the mechanism is dissociative, with the water loss being the dominant step of the process. Consequently, it is interesting to study other dissociative mechanisms in redox reactions (in the solid state), such as the well-known decomposition process of $K_2[Pt(CN)_4X_2]$ (X = Cl, Br, I) [4].

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In this paper we present the study of the kinetics and mechanism of the redox process of decomposition of $K_2[Pt(CN)_4X_2]$ in order to ascertain the influence of redox potentials, free space and crystal field activation energy.

EXPERIMENTAL

Preparation of the compounds

The three salts were prepared by published methods [5,6]. The chloro and bromo complexes are stable at room temperature but the iodo analogue decomposes at room temperature. Consequently thermogravimetric studies must be carried out immediately after synthesis.

TG studies

Thermogravimetric studies were carried out on a Perkin-Elmer model TGS-2 system at a heating rate of 5°C $\min^{-1}$ in a nitrogen atmosphere (non-isothermal measurements). The amount of sample was 6–7 mg. The kinetic parameters were determined on the basis of the general kinetic relation

$$\mathrm{d}\alpha/\mathrm{d}t = k(T)f(\alpha)$$

where $k(T) = k_0 \exp[-E_a/RT]$ (Arrhenius law), k_0 = frequency factor or pre-exponential factor; E_a = activation energy and α = mole fraction. Mathematically, this expression can be converted to

$$\int_0^1 \mathrm{d}\alpha/f(\alpha) = \int_{T_0}^{T_1} k(T)\,\mathrm{d}t = g(\alpha)$$

The main difficulty in solid kinetics is to find the appropriate expression of $g(\alpha)$ or $f(\alpha)$ for each case.

TABLE 1

Kinetic functions, $g(\alpha)$, used in their integral form

Mechanism	$g(\alpha)$
Nucleation-controlled	
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	$[-\ln(1-\alpha)]^{1/n}$
Diffusion-controlled	
One-dimensional	α^2
Two-dimensional	$\alpha+(1-\alpha)\ln(1-\alpha)$
Three-dimensional	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional	$(1-2/3\alpha)-(1-\alpha)^{2/3}$

In this work we have used all the principal expressions of $g(\alpha)$ reported [7] (Table 1), following the four physical models of solid-state chemistry: nucleation, growth, nucleation-growth and diffusion. To find the real kinetic parameters, we have compared the variable values obtained for non-isothermal measurements with the almost constant values for any model by the isothermal method [8]. For the non-isothermal measurements, the expression

$$g(\alpha) = \int k(T)\,\mathrm{d}t$$

was resolved by the widely employed approximation of Coats and Redfern [9]. For the isothermal analysis, the general equation is simply $g(\alpha) = kt$. In this case, isothermal pre-heating at low temperature (50–60°C) was carried out until weight stabilization. All the calculations were made with an ad hoc FORTRAN IV program.

RESULTS

The compound $K_2[Pt(CN)_4Cl_2]$ is completely stable at room temperature. It can be heated to 250–300°C without decomposition. $K_2[Pt(CN)_4Br_2]$ is also stable at room temperature and can be heated to 150–200°C without decomposition. Nevertheless, both products are slightly unstable in air, becoming darker in colour after several days. $K_2[Pt(CN)_4I_2]$ is very unstable at room temperature and decomposes quickly at 100°C.

The non-isothermal TG curves for the first solid phase thermal decomposition of the three salts are given in Fig. 1. For the chloro compound a mass loss of approximately 26 a.m.u. occurred between 300 and 475°C, corresponding to $\frac{1}{2}(CN)_2$. For the bromo compound, a mass loss of 26 a.m.u. occurred between 275 and 425°C, corresponding to $\frac{1}{2}(CN)_2$; for the iodo compound the behaviour is different: a mass loss of 254 a.m.u. occurred between room temperature at 230°C, corresponding to 1 mol of I_2. The isothermal runs confirm the mass loss in each case. These isothermal TG runs were made at four different temperatures for each product. The computational results (in order to work in the same scale) are given in Figs. 2, 3 and 4.

From these results, the analytical and spectroscopic measurements, and the literature data for the bromo compound [4], we can write the first decomposition process as follows

$$K_2[Pt(CN)_4Cl_2] \rightarrow K_2[Pt(CN)_3Cl_2] + \tfrac{1}{2}(CN)_2$$

$$K_2[Pt(CN)_4Br_2] \rightarrow K_2[Pt(CN)_3Br_2] + \tfrac{1}{2}(CN)_2$$

$$K_2[Pt(CN)_4I_2] \rightarrow K_2[Pt(CN)_4] + I_2$$

The structure of $K_2[Pt(CN)_3X_2]$ ($X = Cl$, Br) is unknown. However,

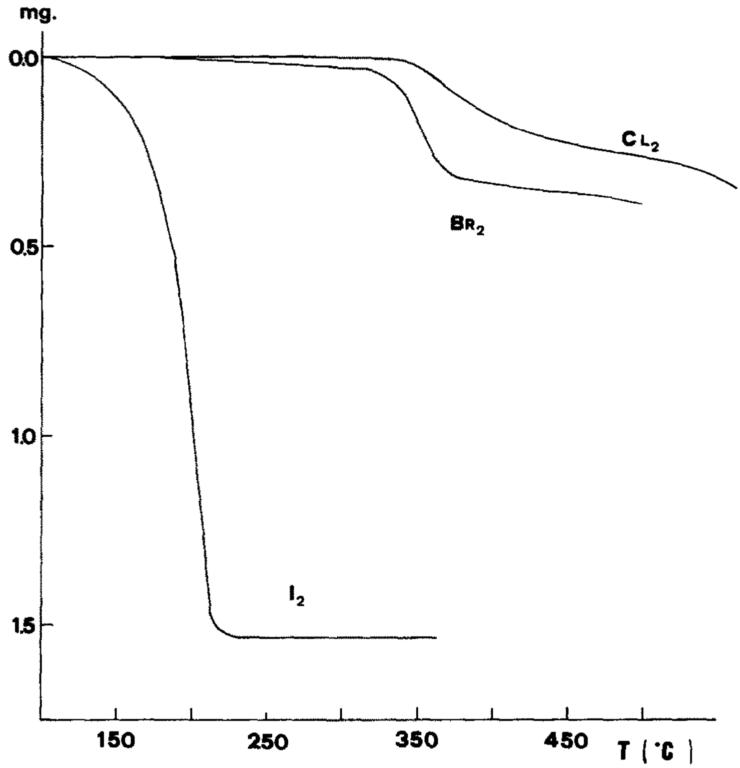

Fig. 1. Non-isothermal TG curves for $K_2[Pt(CN)_4X_2]$ (X = Cl, 4.483 mg; X = Br, 7.432 mg; X = I, 3.829 mg).

considering the IR spectra (indicating the presence of cyanide as bridging and termal ligands), the electronic spectra and the colour (green) and its lack of conductivity, it is reasonable to conclude that the two complexes are one-dimensional mixed-valence complexes of Pt(II)–Pt(IV), bridged by one cyanide ligand.

In order to calculate the kinetic parameters, all the principal expressions of the solid-state decomposition are used (Table 1), both from the isothermal and non-isothermal methods. Many investigations made with non-isothermal methods only, accept or assume the reaction mechanism, i.e. the function $g(\alpha)$ of $f(\alpha)$. In order to avoid these assumptions, we consider that the reaction mechanism may be established by comparing the dynamic and isothermal conditions, as has also been suggested by other workers [7,10]. The advantage of this method is that the mechanism and the order of the reaction is not assumed, and all kinetic parameters are determined from experimental data.

Taking into account that almost none of the decomposition processes of coordination compounds are described in terms of diffusion law, we can expect that these compounds behave according to the growth, nucleation or

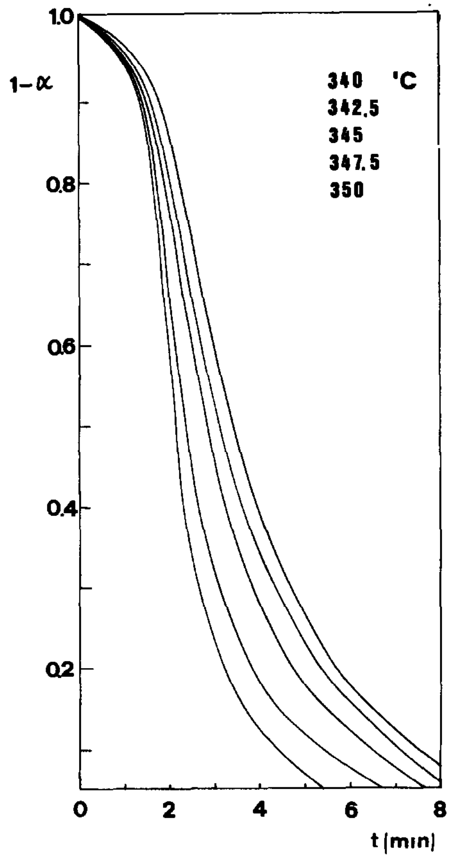

Fig. 2. Isothermal TG curves for $K_2[Pt(CN)_4Cl_2]$. The curves are cut at $\alpha = 0.05$ to avoid lengthening the abscissa.

intermediate laws. Effectively, this means that the E_a, k_0 and r^2 (regression coefficient) values found by us using the diffusion model may not be compared with those obtained by the non-isothermal and isothermal methods [11].

The E_a and k_0 values can be deduced from the isothermal curves, since the values so obtained are almost independent of the physical model proposed [8]. The average kinetic parameters E_a and k_0 are given in Table 2. Taking into account the possible deviation and error of these values we can affirm that the real activation energy of the chloro compound is about 240 kJ mol^{-1}, 245 kJ mol^{-1} for the bromo compound and about 100 kJ mol^{-1} for the iodo compound.

The physical model (nucleation, growth or intermediate) is assigned on the basis of the agreement between the activation parameters from both the non-isothermal and isothermal methods and on the basis of the shape of the isothermal runs. Agreement of the activation parameters, however, is not

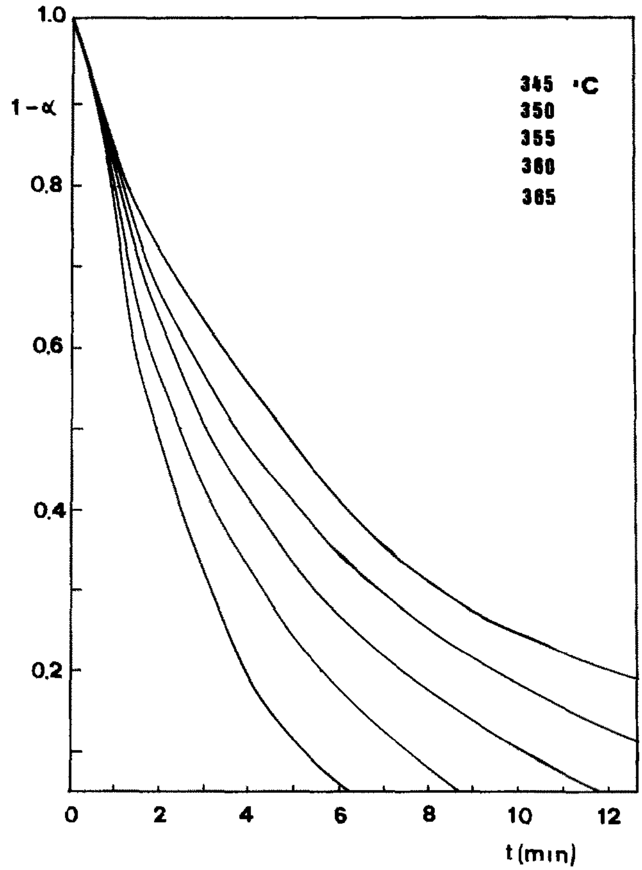

Fig. 3. Isothermal TG curves for $K_2[Pt(CN)_4Br_2]$. The curves are cut at $\alpha = 0.05$ to avoid lengthening the abscissa.

universal: effectively, for the chloro compound there is good agreement for the Avrami law with $n = 1.5$ and for the growth model with $n = 0$ (growth model with $n = 0$ is mathematically equal to the Power law with $n = 1$). For the bromo compound there is a good agreement for the Avrami law with $n = 1$ and for the growth model with $n = 2/3$. In the iodo complex the only coincidence is for the Avrami law with $n = 1$. In the two first cases, r^2 is better for the Avrami law.

TABLE 2

Average kinetic parameters

	E_a	log k_0
$K_2[Pt(CN)_4Cl_2]$	240.5 ± 2	19
$K_2[Pt(CN)_4Br_2]$	245.7 ± 7	18
$K_2[Pt(CN)_4I_2]$	97.5 ± 2	9

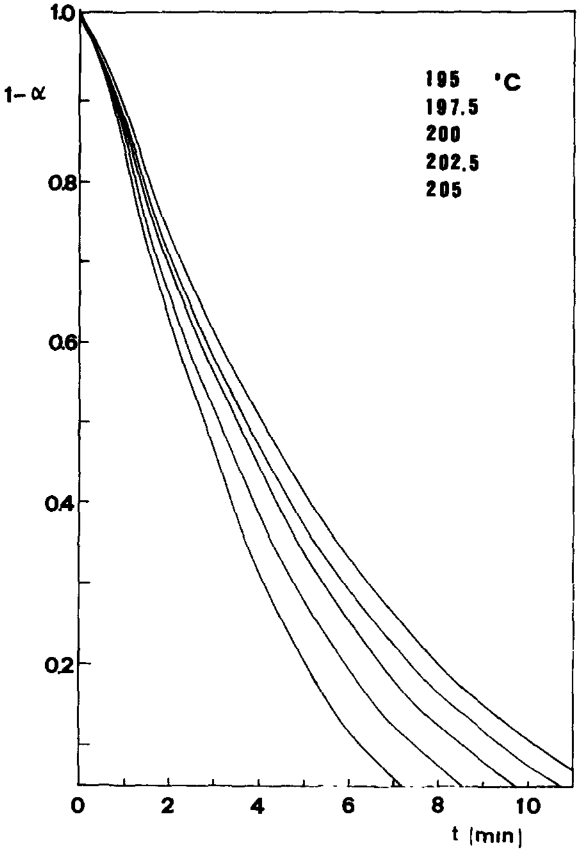

Fig. 4. Isothermal TG curves for $K_2[Pt(CN)_4I_2]$. The curves are cut at $\alpha = 0.05$ to avoid lengthening the abscissa.

Consequently the shape of the isothermal curves is important. Due to the sigmoidal shape of the curves for the three complexes, it is probable that the physical model will correspond to the nucleation-growth model, according to the Avrami law. Previous reports suggest that the sigmoid shape agrees with this law (the greater the sigmoid the higher the n value) [7]. In our case the chloro complex has a pronounced sigmoid shape and corresponds to $n = 1.5$ and the other two compounds have a less pronounced sigmoid shape and correspond effectively to $n = 1$.

DISCUSSION AND MECHANISM

The interpretation of the dominant rate-controlling factor is very complicated in the decomposition of coordination compounds in the solid state. This rate-controlling factor is known only in the simple dehydration–anation processes of octahedral aquaamminecomplexes [1–3]. In these cases loss of the water molecules is precisely the rate-controlling factor, strongly influenced by the free space in the crystal lattice, which allows the water molecule to escape more or less easily.

In the compounds reported here there is no substitution process, but decomposition only. Consequently, the liberation of $(CN)_2$ or I_2 must be the rate-controlling factor.

First it is necessary to ask why the chloro and bromo complexes give $\frac{1}{2}(CN)_2$ whereas the iodocomplex gives I_2. The reduction potentials (in the standard solution) are 1.36 for Cl_2/Cl^-, 1.065 for Br_2/Br^-, 0.535 for I_2/I^- and 0.37 for $(CN)_2/CN^-$. Consequently, the oxidation capacity of Pt(IV) to Pt(II) must be between Br_2/Br^- and I_2/I^-. In the first two cases, it is easier to oxidize CN^- to give $(CN)_2$ and the platinum complex changes to $K_2[Pt(CN)_3X_2]$, a polynuclear localized mixed-valence Pt(IV)–Pt(II) compound, probably one-dimensional with an –NC–Pt(II)–CN–Pt(IV)–CN– array. In the iodo complex however the Pt(IV) oxidizes I^- to I_2 and the product is the known colourless compound $K_2[Pt(CN)_4]$.

The difference between the E_a values for Cl and Br complexes and the iodo compound can be attributed to two causes: (a) the energy for the Pt–CN bond is greater than that for the Pt–I bond (we have observed that the iodo complex loses I_2 even at room temperature); (b) the size ratio "cyanated anion/K^+ cation" follows the order $I > Br > Cl$. Consequently, the free space which permits the loss of I_2 or $(CN)_2$ will be greater in the iodo complex and lower in the chloro compound. If $(CN)_2$ was the gas evolved in all three cases, the order of the activation energies would be normal. But the gas evolved from the iodo complex is I_2, which is very great in size: the E_a values found (100 kJ mol^{-1}) is lower than the expected value.

This anomaly can be explained in terms of the crystal field activation energy (CFAE), postulated by Basolo and Pearson [12]. Effectively, in the iodo complex, for $[Pt(CN)_4I_2]^{2-}$ one mol of I_2 is lost. Consequently, we can expect that the activated species was square-planar and not square-pyramidal (five-coordination), as in the chloro and bromo complexes, which lose only $\frac{1}{2}(CN)_2$. For an octahedral complex to become square-pyramidal requires 4.00 Dq for $d^6(Pt^{IV})$ or 2Dq for $d^8(Pt^{II})$, while to pass to a square-planar configuration, the CFAE is negative in both cases (-5.12 Dq and -12.56 Dq for d^6 and d^8 respectively). In a redox reaction it is very difficult to determine with precision the true Dq, but if the activated complex is square-planar instead of a square-pyramid, the CFAE will have a negative contribution and consequently the E_a will be lower, as in the iodo complex in this case.

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