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Kinetic studies on the thermal dehydration of 4-aminopyridinium (1,2-dithiooxalato-*S*,*S*′)metalate(II) dihydrate complexes (M = Ni, Pd and Pt)

Pascual Román *, Javier I. Beitia, Antonio Luque,
Carmen Guzmán-Miralles

Departamento de Química Inorgánica, Universidad del País Vasco, Apartado 644, E-48080, Bilbao, Spain

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Abstract

The thermal dehydration processes of 4-aminopyridinium (1,2-dithiooxalato-*S*,*S*′)metalate (II) dihydrate (M = Ni, Pd and Pt) have been studied under inert (Ar) and oxidative (Ar + O_2) atmospheres by thermogravimetric (TG,DTG and DTA) and DSC techniques and using non-isothermal conditions. The kinetic analysis of the dehydration curves has been performed applying 21 different rate law expressions for theoretical solid-state models (nucleation, growth, nucleation–growth and diffusion). In both atmospheres, the best fits correspond to random nucleation rate laws. The activation energies obtained are 89.6 kJ mol^{-1} for the Ni compound, 94.1 kJ mol^{-1} for the Pd compound and 85.1 kJ mol^{-1} for the Pt compound in the oxidative atmosphere. In the inert atmosphere, the activation energy values are 101.5, 101.5 and 96.1 kJ mol^{-1} for the Ni, Pd and Pt compounds, respectively. These values are in accord with the fact that the three compounds are isostructural. The DSC curves show sharp endothermic peaks for the dehydration processes of the three compounds in both atmospheres and the dehydration enthalpies were computed from them.

Keywords: Kinetic studies; Thermal dehydration; DSC; Thermogravimetric techniques

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1. Introduction

Transition metal complexes containing sulphur donor ligands represent a growing class of compounds whose chemistry is currently a topic of intense research because of their successful application in many fields such as analytical chemistry, catalysis and

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* Corresponding author.

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magnetochemistry, and their key role in several biological processes [1]. One of these sulphur ligands is the dithiooxalate ligand which shows unique properties due to the presence of four donor atoms and the possibilities of charge delocalization on its atoms; its complexes have been the subject of a recent review [2] which emphasizes approaches to synthesis, stereochemistry, magneto–structural correlations, bonding and reaction chemistry.

On the other hand, in the last few years, a particular aspect of the solid-state chemistry field which has received growing attention is the way in which molecules and ions are organized in the solid-state to form novel materials with improved electrical, optical, magnetic or catalytic properties. Despite important progress in this area, we are still quite a way from being able to design and synthesize specific structural architectures in the solid-state (crystal engineering) which would result in the development of novel materials with characteristic physical and chemical properties. In this respect, there have been theoretical studies on packing interactions in simple organic systems [3] but, so far, very few systematic reports have been published concerning inorganic complexes that investigate the relationships between the characteristics of the individual components (ions or neutral molecules) and the way a crystalline compound is constructed and organized [4]. This research would be of particular importance not only in the field of coordination solid-state chemistry, in which it is a common practice to base the crystallization of new compounds on empirical rules and 'local' recipes [5], but also in many areas such as catalysis and bioinorganic and materials chemistry where coordination complexes play an important role.

In this context, during our study of the chemistry of the 1,2-dithiooxalate (dto) dianion, we have prepared a wide variety of square–planar d^8 metal complexes of the type $(\text{cation})_2[\text{M(dto)}_2]$, where the cations are aromatic planar protonated amines such as pyridine, alkylpyridines and aminopyridines and M may be Ni(II), Pd(II) and Pt(II) [6–10]. In this general research, we are attempting to analyze the influence of features of the organic cation (size, shape and nature and position of the substituents) and the nature of the metal on the packing interactions which govern the crystal organization and – as a consequence – the thermal and chemical properties of this kind of complex. In these studies we have found that this kind of compound shows a laminar structure with the anions and cations arranged almost parallel (mean plane dihedral angles ranging from 1° to 15°) in mixed cation–anion rows; each anion is sandwiched between two cations and each cation has an anion and another cation as nearest neighbours. This arrangement favours the existence of face-to-face interactions between the π systems of the aromatic cations and also between the cation and the dithiooxalate ligands. Inter-row bonding is achieved by means of coulombic forces and by an extensive hydrogen-bond network between the amine groups and the dithiooxalate oxygen atoms from adjacent rows. These hydrogen bonds are made possible by the displacement of each row relative to the nearest ones which enables the *endo*-ammonium pyridine hydrogen and the *exo*-amino substituent hydrogens in the amine derivatives – all of them placed in the plane ring because of the sp^2 hybridation of the *N* atom – to point to oxygen atoms from adjacent anions, lying almost in the same plane, and establish short and nearly linear interactions. This arrangement enables all potential donor hydrogen-bond atoms to form strong $\text{N–H}\cdots\text{O}$ interactions and also favours the existence of hydrophobic regions between two neighbouring cations from adjacent rows. These facts preclude the presence of water of crystallization molecules in these crystal structures. As far as we aware, the (1,2-dithiooxalato-*S*,*S*′)metalate(II) complexes of aromatic cations are usually anhydrous salts, the 4-aminopyridinium salts being the only organic ones containing free water molecules. This may be explained on the basis of the above described crystal packing and the cation features. The presence of two amino groups on opposite sites of the 4-aminopyridinium cation enables it to form hydrogen bonds not only with the dithiooxalate oxygen atoms but also with water molecules which are located in the hydrophilic spaces between two cations from adjacent anion–cation rows [11].

In recent years, there has been increasing interest in determining the rate dependence of solid-state non-isothermal decomposition reactions from an analysis of the thermogravimetric curve. In a previous paper [12], we reported the thermal decomposition of the 4-aminopyridinium (1,2-dithiooxalato-*S*,*S*′)metalate(II) dihydrate complexes ($M = Ni$, Pd and Pt). However, no attempts have been made to investigate the kinetic aspects of the thermal decomposition of these compounds. In the present study, the dehydration steps under inert and oxidative atmospheres are studied by means of non-isothermal kinetic analysis, and the heats of dehydration are quantitatively determined by differential scanning calorimetry.

2. Experimental

2.1. Materials

The compounds studied in this work were all prepared by room-temperature mixing of aqueous solutions of 4-aminopyridinium hydrochloride and the appropriate potassium bis(dithiooxalato)metalate(II) salts according to the method described in a previous paper [11].

2.2. Methods

Thermogravimetric measurements in argon–oxygen and argon atmospheres were carried out according to the procedure described in a previous paper [12]. Calorimetric measurements were performed using a Mettler TA 4000 DSC system, with a $5° \min^{-1}$ heating rate. Enthalpy changes were determined by integration of peak areas after the instrument was calibrated using the fusion of metallic tin.

The kinetic parameters were determined on basis of the general kinetic relationship:

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

where α represents the fraction of reactant decomposed at time t, $f(\alpha)$ is the conversion function of α dependent on the mechanism of the reaction, β is the linear heating rate, dT/dt, and $k(T)$ is the rate constant. The value of $k(T)$ at different temperatures for the same reaction is generally assumed to be governed by the Arrhenius equation.

$$k = A\,\mathrm{e}^{-E_a/RT} \tag{2}$$

where A is the pre-exponential factor, E_a is the activation energy and R is the gas constant.

Combining Eqs. (1) and (2) we obtain:

$$g(\alpha) = \int_0^{\alpha} \frac{\mathrm{d}\alpha}{f(\alpha)} = \int_{T_0}^{T} \frac{A}{\beta}\,\mathrm{e}^{-E_a/RT}\mathrm{d}T \tag{3}$$

and by integration:

$$g(\alpha) = \frac{AE}{R\beta}\,p(x) \tag{4}$$

where

$$p(x) = \int_x^{\infty} \frac{\mathrm{e}^{-x}}{x^2}\,\mathrm{d}x \quad \text{and} \quad x = E/RT \tag{5}$$

This is the basic form of the equation used for analysing non-isothermal data. The expression for $g(\alpha)$ depends on the mechanism of the solid-state reaction: nucleation, growth, nucleation–growth and diffusion. The commonly used $g(\alpha)$ forms of solid state reactions along and the rate controlling processes are given in Table 1.

In order to determine the mechanism and the kinetic parameters (activation energy E_a, frequency factor A and the correlation coefficient r) of the dehydration processes, the (α, t) data from the TG curves, in the range $0.2 \leq \alpha \leq 2.8$, were fitted to the Table 1 rate laws by means of a linear least-squares in-house computer program written in IBM computer FORTRAN. The physical mechanisms were assigned and the corresponding kinetic parameters were calculated on the basis of the higher r^2 values. Three non-mechanistic methods suggested by Coats and Redfern [13, 14], Doyle [15] and Satava [16] were used for comparison.

3. Results and discussion

The results of the thermal studies show that the dehydration of $(HB)_2[M(S_2C_2O_2)_2]_2 \cdot 2H_2O$ (where M is Ni, Pd and Pt, and B is 4-aminopyridine) complexes in argon and argon–oxygen (4:1, v/v) atmospheres takes place in a well defined step between 80 and 140°C. The experimental weight losses and theoretical values for the loss of two molecules of water of crystallization are summarized in Table 2.

As found in the literature for the decomposition of many hydrated compounds [17], the best fits are shown by random nucleation Avrami rate laws of type A 1.5 (Eq. (8) and A 2 (Eq. (9)). The Doyle and Satava methods for random nucleation Avrami rate laws, led to slightly lower r^2 values than those for the Coats–Redfern method. For this reason, only the values obtained from this last method were used for determining the mechanism of these reactions (Table 2).

Table 1
Commonly used forms of $g(\alpha)$ for solid-state reactions along with the rate-controlling processes

Eq. no	Code	Rate-controlling process	From of $g(\alpha)$
(1)	P1	Mampel potential law 1	α
(2)	P2	Mampel potential law 1/2	$\alpha^{1/2}$
(3)	P3	Mampel potential law 1/3	$\alpha^{1/3}$
(4)	P4	Mampel potential law 1/4	$\alpha^{1/4}$
(5)	JE	Johnson equation	$[1/(1-\alpha)]-1$
(6)	A2/3	Random nucleation, Avrami equation 3/2	$[-\ln(1-\alpha)]^{3/2}$
(7)	F1	Random nucleation, one nucleus on each particle, Mampel equation	$[-\ln(1-\alpha)]^{1}$
(8)	A1.5	Random nucleation, Avrami equation 2/3	$[-\ln(1-\alpha)]^{2/3}$
(9)	A2	Random nucleation, Avrami equation 1	$[-\ln(1-\alpha)]^{1/2}$
(10)	A3	Random nucleation, Avrami equation 2	$[-\ln(1-\alpha)]^{1/3}$
(11)	A4	Random nucleation, Avrami equation 1/4	$[-\ln(1-\alpha)]^{1/4}$
(12)	R2	Phase boundary reaction, cylindrical symmetry	$1-(1-\alpha)^{1/2}$
(13)	R3	Phase boundary reaction, spherical symmetry	$1-(1-\alpha)^{1/3}$
(14)	D1	One-dimensional duffusion	α^2
(15)	D2	Two-dimensional diffusion, cylindrical symmetry	$(1-\alpha)\ln(1-\alpha)+\alpha$
(16)	D3	Three-dimensional diffusion, spherical symmetry, Jander equation	$[1-(1-\alpha)^{1/3}]^2$
(17)	D4	Three-dimensional diffusion, spherical symmetry, Brounstein equation	$[1-(2/3)\alpha]-(1-\alpha)^{2/3}$
(18)	D5	Controlled diffusion, Zuralef–Losokhim–Tempelman equation	$[1/(1+\alpha)^{1/3}-1]^2$
(19)	F1.5	Reaction order 1.5	$1/(1-\alpha)^{1/2}$
(20)	F2	Reaction order 2	$1/(1-\alpha)$
(21)	F3	Reaction order 3	$1/(1-\alpha)^2$

Table 2

Thermal analysis data of the $(HB)_2[M(S_2C_2O_2)_2]\cdot 2H_2O$ compounds in Ar + O_2 and Ar atmospheres for the dehydration steps

Compound	Atmosphere	Range/°C	Weight losses/%		Kinetic equation n[a]	Activation energy (kJ mol^{-1})	A	r^2	ΔH/ (kJ mol^{-1})
			Exp.	Theor.					
M = Ni	Ar + O_2	85–140	6.84	6.85	2	89.6	0.28×10^9	0.99940	96.7
	Ar	80–140	7.00	6.85	1.5	101.5	0.15×10^{11}	0.99687	95.8
M = Pd	Ar + O_2	80–130	6.22	6.28	1.5	94.1	0.17×10^{10}	0.99959	99.1
	Ar	90–125	6.14	6.28	2	101.5	0.22×10^{11}	0.99836	100.8
M = Pt	Ar + O_2	80–125	5.77	5.44	2	85.1	0.18×10^9	0.99734	91.1
	Ar	80–130	5.35	5.44	2	96.1	0.71×10^5	0.99919	88.7

[a] $g(\alpha) = [-\ln(1-\alpha)]^{1/n}$.

The activation energy values calculated for the dehydration processes in the oxidative atmosphere are 89.6 kJ mol^{-1} for the Ni compound (random nucleation with $n = 2$), 94.1 kJ mol^{-1} for the Pd compound (random nucleation with $n = 1.5$) and 85.1 kJ mol^{-1} for the Pt compound (random nucleation with $n = 2$) (Table 2).

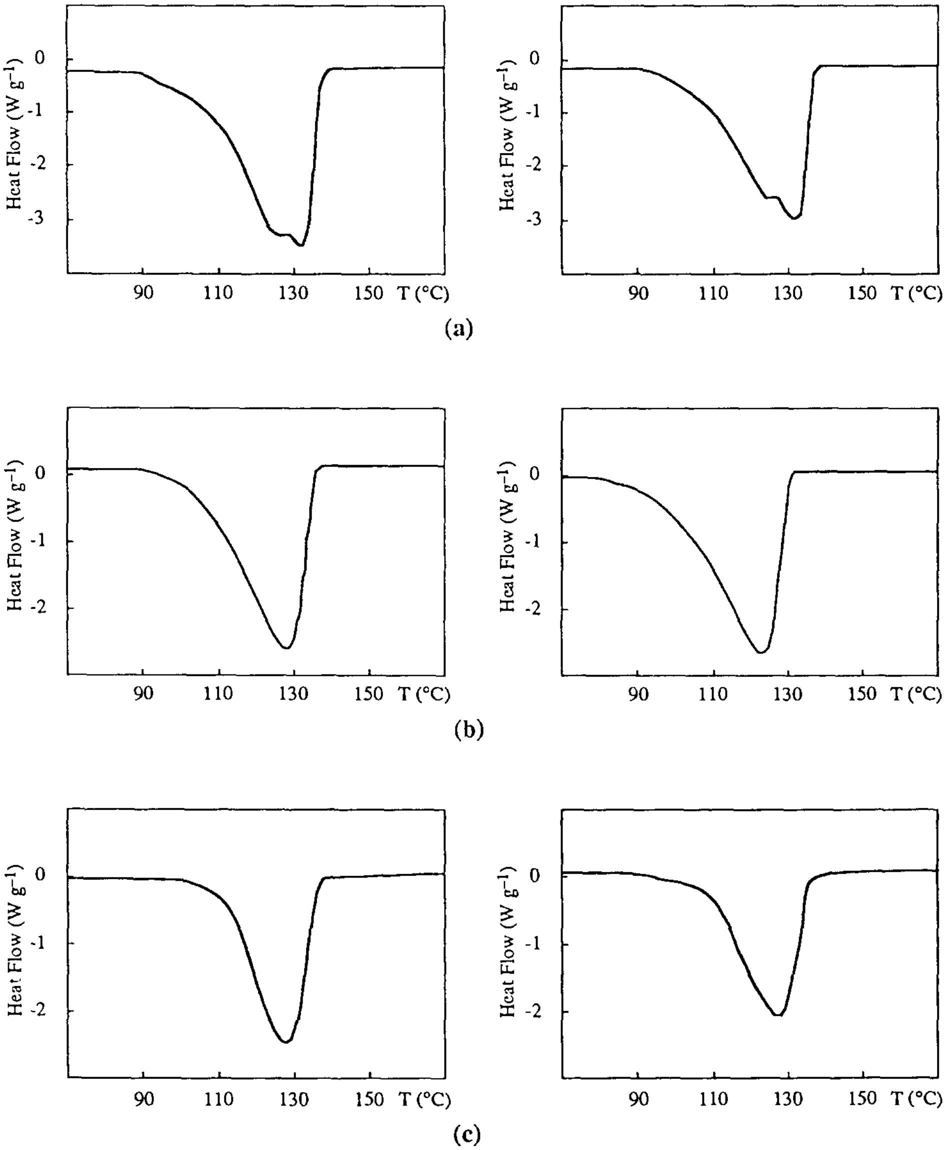

Fig. 1. DSC curves for the complexes: (a) $(HB)_2[Ni(S_2C_2O_2)_2]\cdot 2H_2O$, (b) $(HB)_2[Pd(S_2C_2O_2)_2]\cdot 2H_2O$, and (c) $(HB)_2[Pt(S_2C_2O_2)_2]\cdot 2H_2O$, in argon–oxygen (left) and argon (right) atmospheres.

In the inert atmosphere, the estimated activation energy values are 101.5 kJ mol^{-1} (random nucleation with $n = 1.5$) for the Ni compound and 101.5 and 96.1 kJ mol^{-1} (random nucleation with $n = 2$) for the Pd and Pt compounds, respectively.

The energy values calculated for the dehydration processes for the three compounds are of the same magnitude and are consistent with the fact that the three compounds are isostructural. However, the values obtained in Ar atmosphere are slightly higher that those found in oxidative atmosphere.

The dehydration enthalpies (ΔH) were calculated from the DSC curves (Fig. 1). The values obtained are listed in Table 2. For the Pd and Pt compounds, the DSC curves show that the two water molecules are lost during a single sharp endothermic peak, in accordance with the X-ray single-crystal diffraction analysis [11] that shows that the two water molecules are located in the crystal structure in the same way (they are crystallographically dependent). However, the DSC curve for Ni complex shows two overlapped endothermic peaks which may suggest that the nearly half-dehydrated product reorganizes into a lower hydrate before completing the dehydration process. The total heats of transformation for the three complexes are in good agreement with the value calculated for the heat of dehydration of crystal hydrates ($\Delta H = 45$–55 kJ mol^{-1} H_2O) [18].

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