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THERMAL BEHAVIOR OF Cd^{2+} AND Co^{2+} PHENYL-VINYL-PHOSPHONATES UNDER NON-ISOTHERMAL CONDITION

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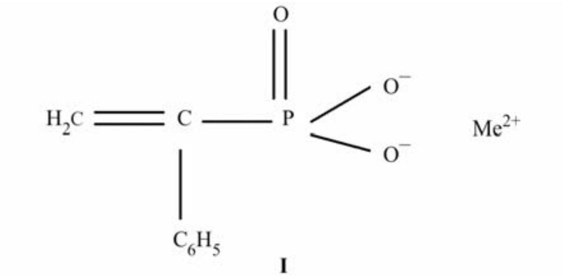
The thermal behavior of Cd^{2+} and Co^{2+} phenyl-vinyl–phosphonates was studied using two different experimental strategies: the coupled TG-EGA (FTIR) technique by decomposition in nitrogen respectively air, and the kinetic analysis of TG data obtained in dynamic air atmosphere at four heating rates. In nitrogen two decomposition steps were observed: the loss of crystallization water, respectively the decomposition of the phenyl-vinyl radical. In air, the same dehydration was observed as the first step, but the second one is a thermooxidation of the organic radical with formation of the pyrophosphoric anion.

The kinetic analysis of the TG non-isothermal data was performed by the isoconversional methods suggested by Friedman and Flynn, Wall and Ozawa, as well as by the non-parametric (Sempere–Nomen) method. All processes put in evidence in TG curves exhibit strong changes of the activation energy values with the conversion degree, which mean that these processes are complex ones. Assuming that each of these processes consists in two steps, the application of non-parametric method leads to average values of the activation energy close to the average values of this parameter obtained by isoconversional methods.

Keywords: *coupled TG-EGA, FTIR spectra, metal phosphonates, non-isothermal kinetics, NPK method*

Introduction

The phenyl-phosphonic acid and its derivatives (**I**) are important as intermediates for ion exchangers, non-linear optical materials, photochemical active materials and hosts intercalation [1].



I

One of the reasons for the interest on these compounds is the wide variety of an accessible structure type: one-dimensional chains [2–4], layered structures [5–7] and three-dimensional microporous frameworks [8, 9].

Despite of the rapid growth of researches on metal phophonates, there are no more reports on the thermal behavior of such compounds. However, the thermal behavior is important for characterizing the intrinsic thermal stability, the working parameters, as well as for obtaining new materials by an adequate thermal treatment.

The topic of the present work is to perform a study under non-isothermal conditions on the thermal behavior of two metal phosphonates (**I**): of Cd^{2+} and Ni^{2+}. The reason for selecting these compounds is in connection with a very recent potential of their use in the hydrogen storage. Indeed, if by a *p*-metal ion the necessary properties for hydrogen storage are not expected, the nickel cation is a favorite. Regarding the organic part, the phenyl-vinyl-radical is the most used for obtaining one-dimensional chains, respectively, layered structures.

Experimental

Synthesis

A solution of phenyl-vinyl phosphonic acid:metal nitrates:urea:water in a molar ratio of 1:1:1:250 was prepared, the pH was adjusted at 2.8 with a 0.1 M solution of NaOH, and then heated 72 h at 70°C. The resulted crystals were filtered and dried in air.

Thermal analysis

The thermoanalytical curves TG, DTG and heat flow were obtained on a Perkin-Elmer Diamond device, using Al crucibles. The experiments were performed

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Table 1 Thermoanalytical data for first step in nitrogen

Sample	*M* (molecular mass)	*a* (relative mass loss)	*x* (No. of water molecule)	max DTG/°C at heating rate of 10°C min^{-1}
MPCd	294	0.060	1.04	180
MPCo	241	0.070	1.01	140

in dynamic atmosphere (100 cm^3 min^{-1}) of nitrogen, respectively air, at heating rates of 5, 7, 10 and 12°C min^{-1} for the kinetic study, respectively, of 20°C min^{-1} for the EGA study.

FTIR spectra

The FTIR spectra were drawn up with a Perkin Elmer Spectrum 100 device, using the U-ATR techniques for the solid phases (compounds before and after the thermal treatment) and an IR–gas cell for the EGA technique. Evolved gases were identified using the Gas Vapor Library (Sadtler Spectral Databases).

Results and discussion

Thermoanalytical data in nitrogen

The thermoanalytical curves of decomposition in nitrogen are depicted in Fig. 1.

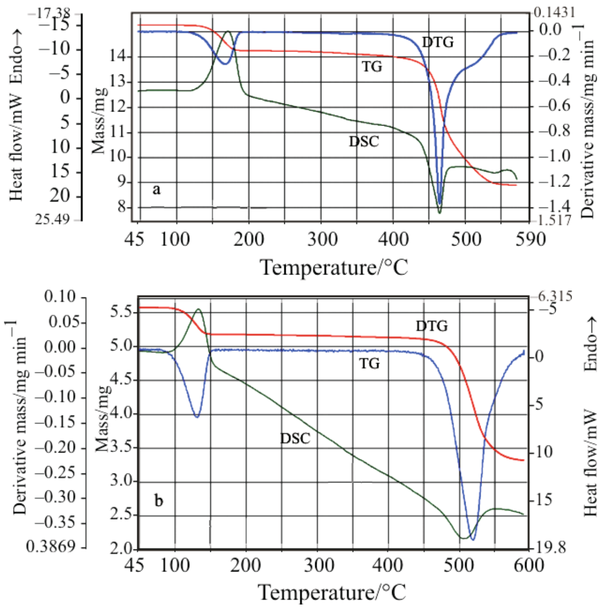


Fig. 1 Thermoanalytical curves for a – MPCd (Cd phenyl-vinyl phosphonates), b – MPCo (Co phenyl-vinyl phosphonates), respectively

There are two well separated processes:

- The first one corresponds to the endothermic mass loss of the crystallization water. The evolved water vapor was identified with the FTIR spectra corresponding to the maximum of the Gramm–Schmidt profile.

The content of crystallization water was determined with the formula:

$$x=\frac{Ma}{18(1-a)} \tag{1}$$

where *M* is the molecular mass of phosphonate without water, *a* – the relative mass loss ($a=\Delta m/m_0$) and *x*– No. of water molecule/phosphonate molecule.

From the data systematized in Table 1 it is obvious that the two compounds are monohydrates.

- The second step corresponds to the destruction of the organic part. The thermoanalytical data are presented in Table 2. The IR spectra of the evolved gas by samples are similar to that of styrene and phenyl-acetylene. So, a thermodegradation with disproportionation of the phenyl-vinyl radical into styrene and phenyl-acetylene is expected.

Table 2 Thermoanalytical data for second step in nitrogen

Sample	T_i/°C	T_f/°C	Δm/mass% (experimental)	max DTG/°C at heating rate of 10°C min^{-1}
MPCd	405	550	29.83	468
MPCo	450	580	32.14	520

Thermoanalytical data in air

The thermoanalytical curves depicted in Fig. 2 indicate also two well separated processes:

- The first one is the water loss of the crystal-hydrates. The maximum of DTG is rather the same as by dehydration in nitrogen. The mass loss is of the same magnitude as by decomposition in nitrogen (Table 1).
- The second step corresponds to a thermooxidative degradation of the organic part (water vapor and carbon dioxide/monoxide by EGA).

In Table 3 the thermoanalytical data for this second step are systematized. However much the DTG maximum would be dependent on the heating rate, by comparison of the corresponding data in Tables 2 and 3, the thermooxidation occurs at temperatures with 80–100°C lower than the thermodegradation in nitrogen. The data

Table 3 Thermoanalytical data of the two steps in air

Sample	Process	T_i/°C	T_f/°C	DTG T_{max}/°C	DTA T_{max}/°C	Δ*m*/mass%
MP-Cd	1	116	176	155	endo 155	5.7
	2	263	452	365	exo 365	24.3
MP-Co	1	111	149	125	endo 130	6.7
	2	376	491	457	exo 457	30.0

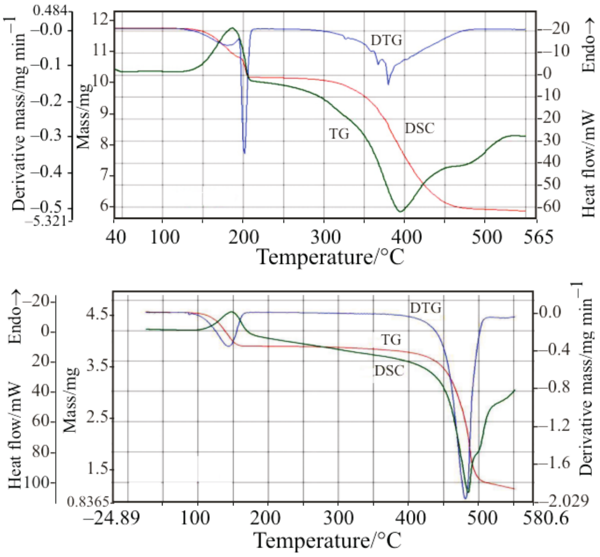
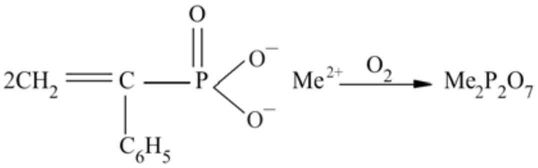


Fig. 2 Thermoanalytical curves for a – Cd, b – Co phenyl-phosphonates in air at heating rates of 20°C min^{-1}, respectively

Table 4 FTIR data of samples before and after thermal treatment

Wavenumber/cm^{-1}	Assignment [10]
Fresh samples	
3466	O–H....O water, crystallization
1400–1350	P=O, free, without H bond
1300–1095	P–C, conjugated
995–985	CHR_1–CH_2
915–905	
740	=CH_2
770–690	$\delta_{(C-H)}$ aromatic ring
After thermooxidation	
1100–950	PO_4^{3-}, $P_2O_7^{4-}$

in Table 4 suggest the formation of pyrophosphate ion, according to the reaction (2).



$$2CH_2{=}C(C_6H_5){-}P(O)(O^-)_2 \; Me^{2+} \xrightarrow{O_2} Me_2P_2O_7 \qquad (2)$$

The experimental mass loss (Table 3 for process No. 2) are with 7–9% lowest than the calculated one, due to an incomplete oxidation under the experimental conditions.

Kinetic analysis

The kinetic analysis for both endo- and exothermic processes in air was performed. Three different methods for TG/DTG data processing were used, i.e. the method by Flynn–Wall [11] and Ozawa [12] (FWO), the method by Friedman [13] respectively the non-parametric kinetic (NPK) method [14–16].

The FWO isoconversional method requires the temperature measurement at certain conversions α for experiments performed at different heating rates β. According to Eq. (3).

$$\ln\beta=\ln\frac{AE}{Rg(\alpha)}-5.331-1.052\frac{E}{RT} \qquad (3)$$

where

$$g(\alpha)=\int_{\alpha_0}^{\alpha} f(\alpha)\mathrm{d}\alpha$$

The value of the activation energy *E* at a certain α will be determined. By this method the conversion function *f*(α) is not explicitly expressed, therefore the FWO method is a model-free method.

- The differential-isoconversional method by Friedman [13]

At constant conversion, the differential form of the reaction rate can be written

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)_{\alpha}=\ln[Af(\alpha)]-\frac{E}{RT} \qquad (4)$$

where β is the heating rate, α – the conversion degree at temperature *T*, *f*(α) – the conversion function and *A*, respectively *E* the pre-exponent factor and the activation energy in the Arrhenius equation. Because *f*(α) is not explicit, Friedman's method is also a 'model free' method.

The data on the variation of *E* *vs*. α are presented in Fig. 3.

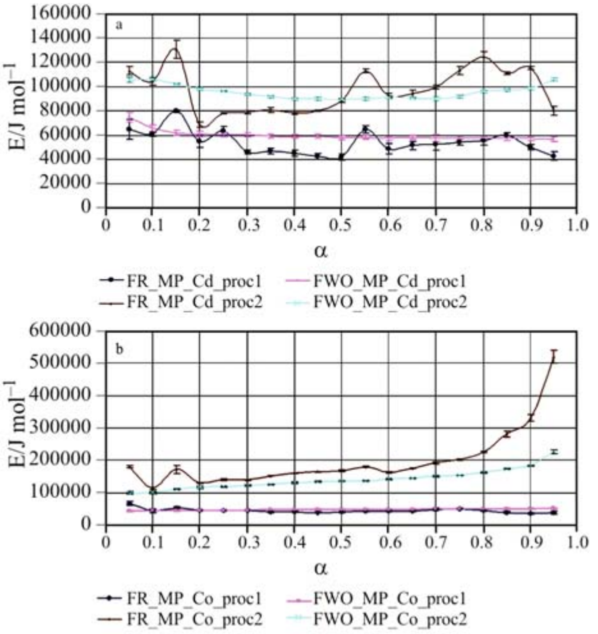


Fig. 3 The variation of activation energy (E) *vs.* conversion degree (α) by Friedman (FR) and Flynn–Wall–Ozawa (FWO) methods for two decomposition processes in air of a – Cd-phenyl-vinyl phosphonate, b – Co-phenyl-vinyl phosphonate

The integral method FWO furnishes a rather parallel variation of E *vs.* α while by differential method (FR) the variation is very non-uniform. Noticeable is the situation for the dehydration step of Co salt: by the both FR and FWO methods the values are identical. The observed differences between the values of the activation energy obtained by the two isoconversional methods are explained by the relations that ground them [17, 18]. The differential Friedman method uses the point values of the overall rate, while Flynn–Wall–Ozawa method uses integrals, which describe the history of the system in the range 0–α.

The significant variation of E *vs.* α obtained by the both mentioned methods suggest a complex process, so a more sophisticated kinetic method was used.

- The non parametric kinetic method [14–16, 19–22]. By this method, the reaction rates $\beta d\alpha/dT$, measured from several experiments at different heating rates, β, were interpolated as a surface in a 3D space ($\beta d\alpha/dT$, α, T). This surface is organized as an x_{ij} matrix M, where the rows correspond to different degrees of conversion α_i, and the columns correspond to different temperatures T_j. Based on the assumption that the reaction rate can be expressed as a product of two independent functions, $f(T)$ and $g(\alpha)$, an element i,j of the matrix M is $M_{i,j}=f(T_j)g(\alpha_i)$.

By the singular value decomposition algorithm [23], the matrix is decomposed according to equation:

$$\mathrm{M}=\mathrm{U}(\mathrm{diag}\mathrm{S})\mathrm{V}^{\mathrm{T}} \qquad (5)$$

A vector u_1 given by the first column of U is analyzed *vs.* α to determine the conversion function; we suggest the Šestak–Berggren equation [24]:

$$g(\alpha)=\alpha^{m}(1-\alpha)^{n} \qquad (6)$$

A similar vector v_1, corresponding to V is checked for an Arrhenius type temperature dependence.

In case of a multi-step process, for example with two simultaneous reactions of rates r_1 and r_2,

$$r=r_1+r_2=f_1(T)g_1(\alpha)+f_2(T)g_2(\alpha) \qquad (7)$$

the initial matrix became

$$\mathrm{M}=\mathrm{M}_1+\mathrm{M}_2 \qquad (8)$$

and the contribution of each step to the observed process is expressed by the explained variance λ, so that $\sum\lambda_i=100\%$.

The data are systematized in Table 5. Only steps with $\lambda\geq10\%$ are considered. The explained variance λ seems the percent from the variation of the experimental data explained by the proposed processes. According to the data in Table 6, in almost all cases the decomposition step are complex: two significant parallel processes, with the reaction rate dependent on amount of both unreacted compound ($n\neq0$), respectively, reaction product ($m\neq0$). Because the final

Table 5 Kinetic analysis by NPK method

Sample	Process	Step	λ/%	E /kJ mol^{-1}	A/min^{-1}	n	m	$\sum\lambda E$
MP-Cd	1	prep	81.8	62.7±8.9	$1.01\cdot10^{7}\pm1.18\cdot10^{3}$	1	1	63.1±8.9
		sec	17.6	67.2±9.4	$6.25\cdot10^{7}\pm6.8\cdot10^{2}$	3/2	2/3	
	2	prep	79.4	80.5±7.7	$7.6\cdot10^{5}\pm6.58\cdot10$	1	1/3	94.6±14.37
		sec	20.4	150.6±40.8	$3.95\cdot10^{11}\pm2.0\cdot10^{8}$	3/2	2/3	
MP-Co	1	prep	87.4	45.28±3.8	$1.46\cdot10^{5}\pm2.3\cdot10$	3/2	2/3	47.7±6.27
		sec	7.6	107.4±38.8	$1.58\cdot10^{13}\pm1.10\cdot10^{12}$	5/3	1	
	2	prep	83.5	190.7±27.5	$8.6\cdot10^{12}\pm3.58\cdot10^{5}$	5/3	1	178.7±27.1
		sec	13.4	145.0±30.6	$1.14\cdot10^{10}\pm2.47\cdot10^{5}$	1/5	–	

Table 6 Comparative value of the activation energy

Sample/process	$E_{a\,(main)}$/kJ mol^{-1}		
	Flynn–Wall–Ozawa	Friedman	NPK ($\sum \lambda E$)
MP – Cd (pr. 1)	63.0±4.1	56.9±9.5	63.1±8.9
MP – Cd (pr. 2)	100.6±5.8	102.3±17.8	94.6±14.37
MP – Co (pr. 1)	51.1±2.2	49.4±8.4	47.7±6.27
MP – Co (pr. 2)	148.9±30.0	191.5±50.0	178.7±27.1

purpose of this paper is to express the thermal behavior of the studied compounds in a synthetic and formal manner, we compared the main values of the activation energy by FR, respectively FWO methods are compared with the $\sum \lambda E$ values by NPK method. We consider that the mean values by NPK method are in a rather good agreement with the other two methods, despite the fact that one is an integral method and the other is a differential one. These mean values are useful for a formal description of the entire process of thermal degradation.

Conclusions

The thermal behavior of Cd^{2+} and Co^{2+} phosphonates was studied in nitrogen, respectively air, under non-isothermal conditions.

The first mass loss step corresponds to the elimination of crystallization water, and takes place at the same temperature range in nitrogen as well as in air.

The second mass loss step corresponds to the elimination of the organic part. The processes are different, depending on the atmosphere: in nitrogen it is a disproportionation of the organic radical, whereas in air it is an oxidation process of both organic radical and phosphonic anion.

The kinetic study of the dehydration and thermo-oxidation processes allows the conclusion that the NPK method leads to average values of activation energy comparable with the average values of this quantity obtained by the considered isoconversional methods.

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