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Non-isothermal kinetics by decomposition of some catalyst precursors

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Abstract

The thermal decomposition of the formates, acetates and propionates of Mn, Ni, Co, Cu, Zn, Cd, La, Eu and Sm were subjected to non-isothermal kinetic study. The observed compensation effect allows us to calculate the isokinetic temperature. A selective activation mechanism was suggested. This led to a good agreement between kinetic and spectroscopic data.

Keywords: Non-isothermal kinetics; Compensation effect; Isokinetic temperature; IR wave number

1. Introduction

The non-isothermal kinetics has been widely used to study the thermal behavior of organic salts and complexes [1]. If the kinetic studies are carried out on a series of similar compounds, one can probe deeper the compensation effect, i.e. the parallel variation of the activation energy and the logarithm of the pre-exponential factor [2].

In the present work the activation energy, the pre-exponential factor, the entropy and enthalpy of activation and the isokinetic parameters have been obtained for the non-isothermal decomposition of some transitional metals carboxylates. These carboxylates are adequate catalyst precursors, due to their low decomposition temperatures. A recent study was performed on the kinetics of the thermal decomposition of copper acetate [3], but it is a lack of information on the thermal behavior of some other d and f acetates and also of formates and propionates.

2. Experimental

The studied compounds are presented in Table 1. All the acetates were available as reagent grade salts. Cu and Zn formates respective propionates were prepared from CuO and ZnO with the corresponding amount of formic respective propionic acid. All the other carboxylates were prepared from the corresponding acetates, by precipitation of the hydroxydes with NaOH, washing the precipitate and treating with the corresponding organic acid.

The molecular formulas were confirmed by the IR spectra recorded in the range of 400–4000 cm^{-1}, with an NICOLET 510 FT-IR spectrometer.

The thermogravimetric curves were recorded in static air atmosphere, with Pt crucible and a heating rates of 2.5, 5 and 10 K min^{-1} in the range 298–773 K, using a MOM Q-1000 Derivatograph coupled to a PC.

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Table 1
The carboxylate-type precursors and characteristics of the dehydrating step

Samples	Initial temperature, T_i (°C)	Final temperature, T_f (°C)	Weight loss calculated, $\Delta m_{\mathrm{theor.}}$ (%)	Weight loss experimental, Δm_{exp} (%)
Formates				
$Cu(HCOO)_2\cdot 2H_2O$	50	78.5	19.1	21
$Zn(HCOO)_2\cdot 2H_2O$	75	115	18.8	18.7
$Mn(HCOO)_2\cdot H_2O$	89	115	11	8.5
$Co(HCOO)_2\cdot 2H_2O$	124	190	19.5	20.1
Acetates				
$Cu(CH_3COO)_2\cdot H_2O$	86	110	8.1	9
$Zn(CH_3COO)_2\cdot 2H_2O$	40	85	16.4	17
$Cd(CH_3COO)_2\cdot 2H_2O$	55	110	13.5	14
$Mn(CH_3COO)_2\cdot H_2O$	50	88	17.5	17.2
$Eu(CH_3COO)_3\cdot 2H_2O$	70	110	9.9	10
$La(CH_3COO)_3\cdot 2H_2O$	52	73	10.2	10.5
$Sm(CH_3COO)_3\cdot 3H_2O$	40	62	9.4	9.5
Propionates				
$Cd(C_2H_5COO)_2\cdot H_2O$	120	195	6.5	5.5
$Sm(C_2H_5COO)_3\cdot 2H_2O$	158	210	8.9	10
$Zn(C_2H_5COO)_2\cdot H_2O$	170	223	7.8	7.5
$Ni(C_2H_5COO)_2\cdot H_2O$	105	168	8.1	8.6
$Cu(C_2H_5COO)_2\cdot H_2O$	108	145	7.9	5.9
$La(C_2H_5COO)_3\cdot H_2O$	75	150	4.8	4.5

The TG diagrams were processed as described in our previous paper [4].

3. Results and discussions

In the most of the TG diagrams only the dehydrating step was well-separated and should be the subject of the kinetic analysis. The characteristics of this first decomposition step are also presented in Table 1, and was confirmed by the disappearance of the IR band at 3400–3500 cm^{-1}.

3.1. Kinetic analysis

The kinetic parameters, i.e. the activation energy E_a and the pre-exponential factor A, were determined by the integral method of Flynn and Wall [5] and Ozawa [6] and are presented in Table 2. With these values, the rate constant k has been calculated by the well-known Arrhenius equation and from the transition state theory [7], the enthalpy ΔH^* and entropy ΔS^* of the transition state have been determined by

$$k_i = \frac{k_B T_i}{h} e^{\Delta S^*/R} e^{-\Delta H^*/RT} \qquad (1)$$

were k_B and h are the Boltzmann and Planck constants, respectively. These activation functions are presented in Table 2.

The values for the increment of enthalpy ΔH^* when going from precursor to the activated complex are in fair concordance with their homologues for activation energy.

3.2. Compensation effect

By inspecting the values in Table 3, parallel variation of both $\ln A$ versus E_a, respectively, ΔS^* versus ΔH^* is observed by each series of carboxylates. It means the presence of a compensation effect, expressed by

$$\ln A = bE_a + c \qquad (2)$$

respectively,

$$\Delta S^* = b'\Delta H^* + c' \qquad (3)$$

An example is presented in Fig. 1.

Table 2
The kinetic and activation parameters for the dehydration of the carboxylates

	$E_a \times 10^{-5}$ (J mol^{-1})	ln A	$\Delta H^* \times 10^{-5}$ (J mol^{-1})	ΔS^* (J mol^{-1} K^{-1})
Formates				
$Cu(HCOO)_2\cdot 2H_2O$	1.810	62.13	1.783	262.42
$Zn(HCOO)_2\cdot 2H_2O$	1.035	31.67	1.005	8.31
$Mn(HCOO)_2\cdot H_2O$	0.749	21.32	0.718	−77.82
$Co(HCOO)_2\cdot 2H_2O$	1.146	30.04	1.113	−6.18
Acetates				
$Cu(CH_3COO)_2\cdot H_2O$	2.050	62.13	2.03	261.62
$Zn(CH_3COO)_2\cdot 2H_2O$	1.140	37.10	1.12	54.21
$Cd(CH_3COO)_2\cdot 2H_2O$	2.800	96.10	2.77	544.59
$Mn(CH_3COO)_2\cdot H_2O$	2.700	92.20	2.68	512.00
$Eu(CH_3COO)_3\cdot 2H_2O$	1.720	53.16	1.69	187.22
$La(CH_3COO)_3\cdot 2H_2O$	1.000	32.31	0.98	14.51
$Sm(CH_3COO)_3\cdot 3H_2O$	2.880	103.00	2.86	602.64
Propionates				
$Cd(C_2H_5COO)_2\cdot H_2O$	1.312	37.70	1.412	57.44
$Sm(C_2H_5COO)_3\cdot 2H_2O$	1.245	28.23	1.203	−26.69
$Zn(C_2H_5COO)_2\cdot H_2O$	0.863	17.71	0.824	−109.95
$Ni(C_2H_5COO)_2\cdot H_2O$	0.516	17.72	0.488	−126.16
$Cu(C_2H_5COO)_2\cdot H_2O$	0.512	12.53	0.482	−150.89
$La(C_2H_5COO)_3\cdot H_2O$	0.650	18.83	0.620	−98.35

This compensation effect is rather a rule in the non-isothermal kinetic [8] as a consequence of the same decomposition mechanism of the series.

From Eqs. (2) and (3), the isokinetic temperatures are obtained

$$T_{iz} = \frac{1}{R} b \tag{4}$$

respectively,

$$T'_{iz} = \frac{1}{b'} \tag{5}$$

In Table 3, these values are compared for the three series of compounds. The agreement of values due Eqs. (4) and (5) is noticeable.

Table 3
The values of the isokinetic temperature (K)

Carboxylates	T_{iz} from E_a and ln A	T_{iz} from ΔH^* and ΔS^*
Formates	308	308
Acetates	314	315
Propionates	509	528

The existence of the compensation effect has been a source of continuos debate [9]. Now a supplementary question appear: which pairs of activation parameters, E_a and A, respectively, ΔH^* and ΔS^* are suitable to lead to a deeper knowledge of the reaction mechanism.

In the next we suggest an activation mechanism which lead to a relationship between ΔS^* and ΔH^* similar with Eq. (3).

3.3. Activation mechanism

- The breaking bond is assimilated with a Morse oscilator [10] coupled non-linear [11] with the harmonic oscillators of the thermic field.
- The decomposition reaction take place in the solid state, i.e. only the vibrational levels are considered.

By means of the vibrational partition functions

$$Z_v = \frac{1}{1 - e^{-x}} \tag{6}$$

the thermodynamic functions of the activated state became [12]

$$H = k_B T^2 \frac{\partial \ln Z_v}{\partial T} \tag{7}$$

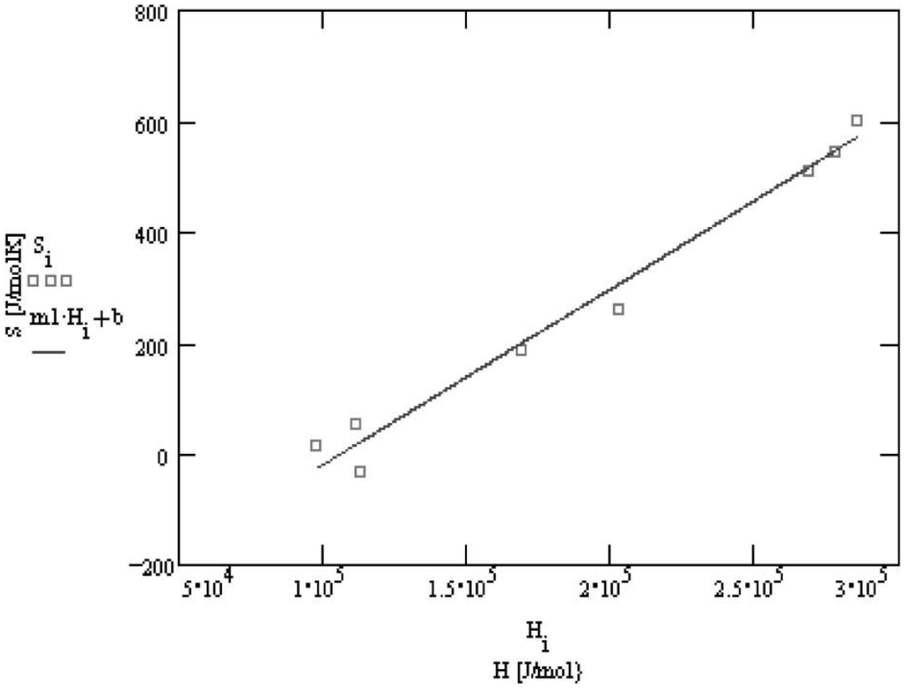

Fig. 1. Compensation effect according to Eq. (3) for all the acetates.

and

$$S = k_B \left[\ln Z_v + T \frac{\partial \ln Z_v}{\partial T} \right] \tag{8}$$

In Eq. (6), $x = \Theta/T$ is dimensionless and is obtained by means of the characteristic temperature

$$\Theta = \frac{hc}{k_B} \omega \tag{9}$$

were c is the light velocity and ω the wave number of the discussed oscillation.

If T_{iz} have an enough high value, $e^x \approx 1 + x$ and consequently $Z_v = 1/x$ and $\partial \ln Z / \partial T = 1/T_{iz}$.

With these suppositions, Eq. (3) became

$$k_B + k_B \ln \frac{T}{\Theta} = k_B \tag{10}$$

i.e.

$$T = \frac{hc}{k_B} \omega \tag{11}$$

According to Eq. (11), the isokinetic temperature can be assimilated with the characteristic temperature of the breaking bond oscillation. This equation allows a correspondence between the kinetic parameter T_{iz} and the spectroscopic one ω. If ω is in cm^{-1} and T_{iz} in K, we obtain

$$\omega_{calc.} = \frac{k_B}{hc} T_i = 0.695 T_i \tag{11a}$$

Because the breaking bond have an unharmonic behavior, the specific activation is also possible due to more than one quanta (or by a higher harmonic)

$$\omega_{sp} = n\omega_{calc.}, \quad n \in N \tag{12}$$

were ω_{sp} is the assigned spectroscopic wave number for the bond supposed to break.

In this paper we analyzed only the dehydration step, so that $\omega_{sp} = 3400\text{–}3500\ \text{cm}^{-1}$. Table 4 presents the $\omega_{calc.}$ obtained with the T_{iz} values in Table 3, also the n value according to Eq. (12). The studied carboxylates exhibit a very good agreement between the wave number calculated from the isokinetic temperature and the corresponding wave number accepted by the IR spectroscopy for the crystallization water.

Table 4
Comparison between the calculated and the assigned IR wave number

Carboxylates	Assignment for water loss ω_{sp} (cm^{-1})	$\omega_{calc.}$ Eq. (11a)	Ascribed value for n	Conclusions $\omega_{calc.}n$
Formates	3400–3500	214	16	3424
Acetates	3400–3500	219	16	3504
Propionates	3400–3500	367	9	3303

4. Conclusions

The kinetic analysis of the non-isothermal dehydration of formates, acetates and propionates of some d and f metals allows the evidence of a compensation effect. The two different equations, i.e. ln A versus E_a and ΔS^* versus ΔH^* lead to quite near values for the isokinetic temperature. But only by means of the thermodynamic functions of the activated complex, it is possible a correlation between the isokinetic temperature and the wave number assigned to the breaking bond.

By the thermal decomposition of solid compounds, the activated state is attained by exciting only the vibrational levels. If the compound are similar and the reaction mechanism identical, a discrete variation of the activation energy values is expected.

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