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DECOMPOSITION OF ORGANIC SALTS OF SOME *d* AND *f* METALS

Non-isothermal kinetics and FT-IR studies

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Abstract

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

Keywords: compensation effect, IR wave number, isokinetic temperature, non-isothermal kinetics

Introduction

The non-isothermal kinetics has been widely used to study the thermal behavior of organic salts and complexes [1]. In our previous paper [2], the dehydration of formates, acetates and propionates of some *d* and *f* metals was studied by means of the non-isothermal kinetic and the observed compensation effect was related to reaction mechanism.

In the present paper we continue the kinetic studies concerning the decomposition step of *d* and *f* metals, including besides formates, acetates, and propionates also butyrates.

Experimental

The studied compounds are presented in Table 1. All the acetates were available as reagent grade salts. Zn and Cu formates, propionates and butyrates were prepared from ZnO and CuO with the corresponding amounts of organic acids. All the other carboxylates were prepared from the corresponding acetates, by precipitation of the hydroxides with NaOH, washing the precipitate and treating it with the corresponding organic acids.

IR spectra were recorded in the range of 400–4000 cm^{-1} with a NICOLET-510 FT-IR Spectrometer.

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Table 1 The compounds and characteristics of the decomposition step

Samples	Mass loss calculated $\Delta m_{\mathrm{theor}}$/mg	Mass loss experimental by different heating rates Δm_{exp}/mg			
		2.5 K min^{-1}	5 K min^{-1}	10 K min^{-1}	20 K min^{-1}
Formates					
$Zn(HCOO)_2$	37.0	–	34.0	34.0	34.5
$Cu(HCOO)_2$	38.5	–	34.0	37.0	36.0
$Ni(HCOO)_2$	17.0	–	16.0	17.0	20.0
$Co(HCOO)_2$	41.0	–	40.0	43.0	41.0
Acetates					
$Mn(CH_3COO)_2$	45.3	45.5	45.0	46.4	–
$Zn(CH_3COO)_2$	30.6	–	41.0	39.5	40.6
$Sm(CH_3COO)_3$	26.4	27.8	25.0	25.2	–
$Eu(CH_3COO)_3$	25.5	–	23.6	24.0	26.5
$Cd(CH_3COO)_2$	39.3	37.0	36.3	37.7	–
Propionates					
$Cd(C_2H_5COO)_2$	28.5	30.5	–	27.5	28.5
$Mn(C_2H_5COO)_2$	45.3		45.6	45.5	44.0
$Zn(C_2H_5COO)_2$	66.0	64.0	–	71.0	66.0
$Ni(C_2H_5COO)_2$	31.0	30.0	–	34.8	33.6
$Cu(C_2H_5COO)_2$	58.9	59.5	–	56.8	56.5
Butyrates					
$Cu(C_3H_7COO)_2$	56.0	–	55.9	55.8	56.8
$Ni(C_3H_7COO)_2$	50.0	–	48.0	50.0	50.9
$Sm(C_3H_7COO)_3$	20.4	–	17.0	22.2	24.0
$Zn(C_3H_7COO)_2$	70.3	–	71.5	70.0	70.5

The thermogravimetric curves were recorded in static air, with Pt crucible and heating rates of 2.5, 5, 10 and 20 K min^{-1} in the range 25–500ºC, using a MOM Q-1000 Derivatograph.

TG data were interpolated with logistical function and finally numerical derivated. With the values of α, $\beta(\mathrm{d}\alpha/\mathrm{d}T)$ and T, the Friedman`s method for estimating the non-isothermal kinetic parameters was used.

Results and discussions

The TG curves of the carboxylate exhibit two steps: the first corresponds to the dehydration and was analyzed in our previous work [2], the second step corresponds to the decomposition of the carboxylates and should be the subject of the present kinetic analysis. The characteristics of this second step are presented in Table 1. The theoretical mass was calculated for the decomposition of carboxylates to carbonates, and by inspecting the data in Table 1, there is a very good agreement between the theoretical and experimental mass loss.

Kinetic analysis

From the generally accepted equation of the non-isothermal kinetics [3]

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}=f(\alpha)\,A\exp\left(-\frac{E}{RT}\right) \tag{1}$$

where β is the heating rate and T is the temperature in K, the equation corresponding to the Friedman's differential isoconversional method, was obtained

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)=\ln[Af(\alpha)]-\frac{E}{RT} \tag{2}$$

For $\alpha = ct$ and using various heating rates, the plot $\ln[\beta(\mathrm{d}\alpha/\mathrm{d}T)]$ *vs.* $(1/T)$ should be linear. From the slope and the intercept of the straight line the value of activation energy and product $[Af(\alpha)]$ were obtained. This enable $E(\alpha)$ and $A(\alpha)$ to be estimated using various values of α (Table 2).

The procedure is based on the following assumptions [4–6]:

1) E and A depend on the degree of conversion and do not depend on the heating rate

2) E and A are correlated through the compensation effect (CE)

$$\ln A=aE+b \tag{3}$$

3) The dependence of E on the degree of conversion is given by

$$E=E_0+E_1\ln(1-\alpha) \tag{4}$$

were E_0 and E_1 are constants.

4) The differential conversion function, $f(\alpha)$ has the form

$$f(\alpha)=(1-\alpha)^{n} \tag{5}$$

From the differential conversion function (5) it follows that

$$\ln[Af(\alpha)]=\ln A+n\ln(1-\alpha) \tag{6}$$

and from the values of $[Af(\alpha)]$ and α, the values of $\ln A$ corresponding to various values of n can be obtained. The plot of $\ln A$ *vs.* E should be linear as required by the existence of compensation effect (Eq. 3). The correct value of n will be the one that gives a correlation coefficient closest to 1.00 for the straight line $\ln A$ *vs.* E.

The presence of the kinetic compensation effect presumes the existence of an isokinetic temperature which can be estimated from the slope of the straight line $\ln A$ *vs.* E.

$$T_{\mathrm{i}}=\frac{1}{R\,a} \tag{7}$$

From Eqs (1–5) we obtain:

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right)=\left(b+aE_0-\frac{E_0}{RT}\right)+\left(aE_1-\frac{E_1}{RT}+n\right)\ln(1-\alpha) \tag{8}$$

Values of the activation energy obtained according Eq. 2 by three heating rates at different reaction degrees are presented in Table 2. A significant variation of *E vs.* α is observed. By means of the kinetic analysis discussed before (Eqs 2–8), the data in Table 3 were obtained. The reaction order was tested for values between 0.1–2.0, with the step of 0.1.

Table 2 Activation energy (kJ mol^{-1}) obtained by Friedman`s method for three heating rates

Compound/α	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$Zn(HCOO)_2$	15.8	17.1	19.5	21.3	24.8	30.0	38.7	54.7	90.0
$Cu(HCOO)_2$	–	218.9	170.9	146.0	129.1	113.6	102.4	88.2	70.6
$Ni(HCOO)_2$	89.7	77.9	68.0	61.3	51.5	43.6	35.4	28.6	27.2
$Co(HCOO)_2$	112.3	97.0	84.2	72.2	63.3	55.2	48.1	38.6	–
$Mn(CH_3COO)_2$	92.5	84.3	79.4	76.9	74.6	72.8	72.0	70.9	71.3
$Zn(CH_3COO)_2$	55.9	59.5	62.5	65.4	68.7	72.7	77.4	83.5	92.0
$Sm(CH_3COO)_3$	–	203.9	159.4	141.0	132.4	128.4	127.9	129.4	132.6
$Eu(CH_3COO)_3$	42.8	43.9	44.5	44.8	45.0	45.0	44.8	–	–
$Cd(CH_3COO)_2$	45.5	44.9	45.0	45.1	46.7	48.2	50.8	56.1	70.5
$Cd(C_2H_5COO)_2$	105.4	93.5	87.6	83.3	79.0	74.9	69.7	60.4	40.2
$Mn(C_2H_5COO)_2$	166.6	134.1	119.0	107.1	100.8	95.1	91.4	89.9	–
$Zn(C_2H_5COO)_2$	44.0	54.9	63.5	71.2	78.6	85.5	92.8	99.8	–
$Ni(C_2H_5COO)_2$	170.9	193.2	202.1	201.0	186.9	170.9	122.2	62.8	–
$Cu(C_2H_5COO)_2$	–	–	92.8	95.1	96.2	96.4	94.6	89.9	78.1
$Cu(C_3H_7COO)_2$	147.3	150.2	150.6	149.3	145.2	140.1	130.8	116.3	87.7
$Ni(C_3H_7COO)_2$	–	487.5	452.9	396.4	299.2	227.1	121.1	68.8	–
$Sm(C_3H_7COO)_3$	–	127.8	139.0	146.5	149.8	148.3	138.7	106.9	–
$Zn(C_3H_7COO)_2$	77.8	82.2	78.1	76.9	79.3	74.7	78.9	–	–

Specificity by non-isothermal decomposition

The specificity by decomposition under non-isothermal conditions is due to a selective vibrational energy accumulation on a certain bond. This breaking bond is assimilated with Morse oscillators [7] coupled non-linear [8] with the harmonic oscillators of the thermic field. Following a theoretical treatment developed in our paper [2], a correspondence will be established between the kinetic parameter T_i and the wave number of the activated bond:

$$\omega_{calc} = \frac{k_B}{hc} T_i = 0.695\, T_i \tag{9}$$

with k_B, h – the Boltzmann, respective Planck constants, and c – the light velocity.

Because the breaking bond has an unharmonic behavior, the specific activation is possible also due to more than one quanta, or by a higher harmonic: $\omega_{sp} = q\omega_{calc}$, $q \in \mathbf{N}$ were ω_{sp} is the assigned spectroscopic number for the bond supposed to break.

In order to corroborate the calculated data with the spectroscopic ones, we drew up the FT-IR spectra of the studied compound.

Table 3 Kinetic parameters according with Eqs (2–8)

Compounds	E_0/kJ mol^{-1} Eq. (4)	E_1/kJ mol^{-1} Eq. (4)	$a\cdot10^4$/mol J^{-1} Eq. (6)	b Eq. (6)	n	Corr. coeff.
$Zn(HCOO)_2$	5.9	–32.7	2.40	–1.5	0.1	0.998
$Cu(HCOO)_2$	189.2	60.6	3.10	0.28	1.0	0.99999
$Ni(HCOO)_2$	78.37	28.0	2.29	0.25	0.8	0.99992
$Co(HCOO)_2$	100.4	40.1	2.07	–0.06	0.6	1.00
$Mn(CH_3COO)_2$	82.7	8.7	2.05	1.14	0.7	0.99999
$Zn(CH_3COO)_2$	56.5	–16.3	3.40	–8.29	2.0	0.99955
$Sm(CH_3COO)_3$	166.1	22.3	2.30	–3.31	0.6	0.99999
$Eu(CH_3COO)_3$	43.6	–1.5	5.90	–17.96	0.2	0.9986
$Cd(CH_3COO)_2$	42.7	–7.2	2.21	–0.98	0.6	0.997
$Cd(C_2H_5COO)_2$	99.9	26.02	2.37	–4.11	0.1	0.997
$Mn(C_2H_5COO)_2$	142.6	42.18	2.34	–0.55	1.3	0.99994
$Zn(C_2H_5COO)_2$	48.7	–35.7	2.65	–3.5	1.5	0.9999
$Ni(C_2H_5COO)_2$	220.3	80.54	2.31	1.37	2.0	0.99993
$Cu(C_2H_5COO)_2$	100.5	7.99	2.59	–1.27	0.8	0.99977
$Cu(C_3H_7COO)_2$	28.3	160.0	2.49	–0.82	0.7	0.9999
$Ni(C_3H_7COO)_2$	523.5	301.2	2.22	0.007	2.0	0.99974
$Sm(C_3H_7COO)_3$	148.7	15.2	2.07	–0.96	0.8	0.99984
$Zn(C_3H_7COO)_2$	79.3	1.84	2.22	–2.45	0.4	0.995

The studied process is a decomposition of carboxylic salts, i.e. a destruction of the carboxylic group. It is reasonable to assume an activation process due to the selective energy absorption by the carboxylate group. The wave numbers accepted by the IR spectroscopy for vibrations of the carboxylate group are in the range of 1330–1440 respectively 1550–1650 cm^{-1}. With the integer q (rather low), the $q\ \omega_{calc}$ values lie in one or both these ranges.

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

Sample	T_i/K Eq. (7)	ω_{calc}/cm^{-1} Eq. (9)	q	$q\omega_{calc}$	ω_{sp}/cm^{-1} present in FT-IR spectra and assignements [9, 10]
$Zn(HCOO)_2$	504.0	350.3	4	1401	
$Cu(HCOO)_2$	387.3	269.3	5	1346	
$Ni(HCOO)_2$	523.5	363.8	4	1455	
$Co(HCOO)_2$	579.9	403.0	4	1612	1330–1440
$Mn(CH_3COO)_2$	586.5	407.6	4	1630	
$Zn(CH_3COO)_2$	349.5	242.9	6	1457	1550–1650
$Sm(CH_3COO)_3$	522.0	362.8	4	1451	
$Eu(CH_3COO)_3$	204.6	142.2	10	1422	
$Cd(CH_3COO)_2$	544.0	378.1	4	1512	
$Cd(C_2H_5COO)_2$	508.0	353.1	4	1412	
$Mn(C_2H_5COO)_2$	514.2	357.4	4	1429	
$Zn(C_2H_5COO)_2$	453.8	315.4	5	1577	
$Ni(C_2H_5COO)_2$	519.8	361.3	4	1445	
$Cu(C_2H_5COO)_2$	464.5	322.5	5	1612	
$Cu(C_3H_7COO)_2$	483.0	335.7	4	1342	
$Ni(C_3H_7COO)_2$	542.5	377.0	4	1508	
$Sm(C_3H_7COO)_3$	581.0	403.8	4	1615	
$Zn(C_3H_7COO)_2$	540.7	375.8	4	1503	

Conclusions

The kinetic analysis of the non-isothermal decomposition of *d* and *f* metal carboxylates allows the evidence of a compensation effect. A correlation between the isokinetic temperature and the wave number of the activated group responsible for the molecule destruction was possible.

Under non-isothermal conditions, the activation/decomposition process is due to a non-linear coupling between different specific oscillators of the solid compound and the continuous spectrum of thermally induced oscillators. The activated state is attained by exciting only the vibrational energy levels. This kind of data processing allows a less-speculative interpretation of the kinetic data. Obviously, the difference between the exactness of the spectroscopic respectively kinetic data, must be taken into account.

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