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SPECIFICITY OF DECOMPOSITION OF SOLIDS IN NON-ISOTHERMAL CONDITIONS

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Abstract

The thermal stability of the food additives Na metabisulphite, Na and K acetates, glutamic and citric acids, respective of the pharmaceuticals nifedipine and acetyl salicylic acid was studied by means of the non-isothermal kinetic (Friedman differential method).

The specificity of the thermal decomposition was characterized by identification of the bond to be selective activated due to energy absorption at vibrational level. These bonds were assigned by comparison of calculated wave numbers with the wave number of the IR spectra.

Keywords: compensation effect, IR wave number, isokinetic temperature, non-isothermal kinetics, pharmaceutical and food additives

Introduction

Many years ago the thermal analysis earned its place as a current instrumentation technique in assisting the analytical problems of pharmaceuticals [1]. A relative new trend in this field is the study of the thermal stability of pharmaceuticals and food additives in connection with the molecular architecture.

In an earlier paper [2] we suggested a correlation between the isokinetic temperature and the wave number assigned to the bond responsible for the beginning of the thermal decomposition of a certain compound. In this paper we extend this study to some usual food additives and pharmaceuticals.

Experimental

The thermal curves were recorded with a MOM Derivatograph devices in static air atmosphere. For the thermal analysis, 100 mg samples were used, with heating rates of 20, 10, 5 and 2.5 K min^{-1}.

The IR spectra were determined in KBr tablet for the initial, respectively the thermal treated samples, using a NICOLET-510 FTIR Spectrometer.

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

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Results and discussion

In Table 1 the main characteristics of the thermal decomposition steps of the studied compounds are systematized.

Table 1 Decomposition characteristics of the studied compounds, determined at different heating rates

No.	Compound	Thermal effect	Mass loss/% by heating rate of °C min^{-1}				Calculated mass loss/%
			20	10	5	2.5	
1	$Na_2S_2O_5$	Exo	25.7	24.5	23.4	24.1	25.0 (Eq. 1)
2a	$Na(CH_3COO)$	Exo	37.0	33.3	33.3	33.9	35.4
2b	$K(CH_3COO)$		28.5	29.0	31.1	30.8	29.5 (Eq. 2)
3	Glutamic acid	Endo	11.8	11.5	11.5	12.9	12.2 (Scheme 1)
4	Citric acid	Endo	83.5	83.0	84.5	81	78.2
5	Nifedipine	Exo	58.0	57.2	55.4	54.3	–
6	Acetylsalicylic acid	Endo	36.5	35.7	36.4	37	33.0

The sodium metabisulphite presents a single important step, an exothermic process with mass loss and without an 'a priori' melting. This step is assigned to a decomposition/oxidation process:

$$Na_2S_2O_5 \rightarrow Na_2SO_3+SO_2 \quad (1)$$

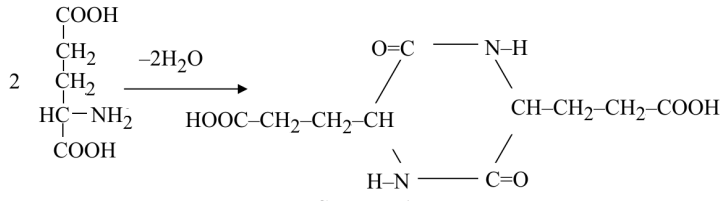
The concordance between the experimental and the calculated mass loss is very good.

The alkaline acetates presents (after dehydration) an exothermic process with mass loss, corresponding to a decomposition according to the equation

$$2M(CH_3COO) \rightarrow 2MCO_3+(CH_3)_2CO \quad (2)$$

The experimental determined mass loss is in very good agreement with the calculated values.

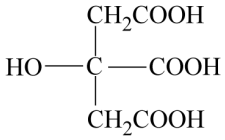
The glutamic acid presents a decomposition step with a significant change in the molecular structure, i.e. the dimerization to dicetopiperazine (Scheme 1).



Scheme 1

This step is endothermic and the determined mass loss agrees very well with the calculated ones.

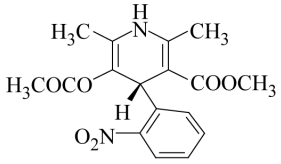
The citric acid presents a melting step with the endothermic maximum at 140ºC. After this, a unique degradation step occurs, with the characteristics presented in Table 1. The theoretical mass loss was calculated for a combined dehydration/decompo-



Scheme 2

sition process, i.e. for the elimination of one water molecule and three carbon dioxide molecules per citric acid molecule.

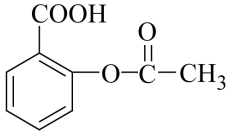
The nifedipine presents a melting step with the endothermic maximum between



Scheme 3

110–150ºC. The decomposition occurs due to the oxidation process with maximum in the range 200–240ºC.

The acetyl salicylic acid presents a first decomposition step with rate maximum between 110 and 140ºC (dependent on heating rate). A relatively good accordance



Scheme 4

exists between the experimental mass loss and that one determined for the elimination of acetic acid.

Kinetic analysis

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

$$\beta \frac{\mathrm{d}\alpha}{\mathrm{d}T} = f(\alpha) A \exp\left(-\frac{E}{RT}\right) \tag{3}$$

(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

Table 2 Activation energy ($E10^{-5}$ J mol^{-1}) obtained by Friedman method for heating rates of 2.5, 5, 10 and 20 K min^{-1}

Compound	α								
	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
$Na_2S_2O_5$	0.64	0.68	0.70	0.71	0.71	0.70	0.67	0.62	0.51
$Na(CH_3COO)$	0.21	0.18	0.16	0.15	0.13	0.12	0.10	0.08	–
$K(CH_3COO)$	3.08	4.16	5.27	6.16	8.13	10.10	11.90	8.72	–
Glutamic acid	0.66	0.62	0.61	0.60	0.61	0.63	0.66	0.75	1.15
Citric acid	1.87	1.67	1.56	1.49	1.43	1.40	1.40	–	–
Nifedipine	1.08	1.18	1.22	1.25	1.24	1.21	1.12	0.96	0.58
Acetylsalicylic acid	0.56	0.59	0.62	0.64	0.66	0.67	0.68	0.68	0.49

$$\ln\left(\beta\frac{d\alpha}{dT}\right)=\ln[A\cdot f(\alpha)]-\frac{E}{RT} \quad (4)$$

For $\alpha=ct$ and using various heating rates, the plot $\ln\left(\beta\frac{d\alpha}{dT}\right)$ *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.

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)

$$\ln A=aE+b \quad (5)$$

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

$$E=E_0+E_1\ln(1-\alpha) \quad (6)$$

where E_0 and E_1 are constants.

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

$$f(\alpha)=(1-\alpha)^n \quad (7)$$

From the differential conversion function (7) it follows that

$$\ln[Af(\alpha)]=\ln A+n\ln(1-\alpha) \quad (8)$$

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. (5)). The correct value of n will be the one which 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.

$$T_i=\frac{1}{Ra} \quad (9)$$

From Eq. (3)–(7) we obtain:

$$\ln\left(\beta\frac{d\alpha}{dT}\right)=\left(b+aE_0-\frac{E_0}{RT}\right)+\left(aE_1-\frac{E_1}{RT}+n\right)\ln(1-\alpha) \quad (10)$$

The values of the activation energy obtained according to Eq. 4 by four 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 (Eq. (5)–(10)), 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 3 Kinetic parameters according to Eq. 10

Compound	E_0/ kJ mol^{-1}	E_1/ kJ mol^{-1}	$a\cdot10^4$/mol J^{-1} (Eq. 5)	b (Eq. 5)	n	Correlation coefficient
$Na_2S_2O_5$	72.5	6.9	3.12	–3.03	0.3	0.9992
$Na(CH_3COO)$	19.3	7.2	1.41	1.83	1.6	0.9992
$K(CH_3COO)$	660.0	22.3	1.79	1.07	1.9	0.9999
Glutamic acid	51.9	–20.4	2.16	0.18	0.1	0.998
Citric acid	171.0	25.8	2.96	–4.72	1.2	0.99996
Nifedipine	131.0	25.0	2.37	–0.96	0.9	0.9998
Acetylsalicylic acid	63.7	1.6	3.09	–2.64	1.5	0.998

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 a Morse oscillators [7] coupled non-linear [8] with the harmonic oscillators of the thermic field. Following a theoretical treatment developed in our papers [2, 9], a correspondence will be established between the kinetic parameter T_i and the wave number of the activated bond:

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

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: $\omega_{sp} = q\omega_{calc}$, $q \in N$, where 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.

In Table 4 the ω_{calc} values with the ω_{sp} determined from the spectra, together with the assignments of the corresponding oscillations are compared. The studied compounds exhibit a very good agreement between the wave number calculated from the isokinetic temperature and the corresponding wave number accepted in IR spectroscopy for the bonds suggested to be broken.

Conclusions

The kinetic analysis of the decomposition of some food additives and pharmaceuticals, under non-isothermal conditions, allows the evidence of a compensation effect, for the kinetic data at different heating rates. By means of the thermodynamic functions of the activated complex, a correlation between the isokinetic temperature and the wave number assigned to the breaking bond is possible. It is possible to ana-

Table 4 Comparison between kinetic and spectroscopic data

Samples	T_i/K Eq. (9)	ω_{calc}/cm^{-1} Eq. (11)	q	$q\omega_{calc}$	ω_{sp}/cm^{-1} present in FT-IR spectra and the assignments [10, 11]
$Na_2S_2O_5$	385	268	4 6	1072 1608	900–1000 1600–1620 bisulphite anion
$Na(CH_3COO)$	851	591	2 3	1182 1773	1330–1440 C=O ν_s by carboxyl anions
$K(CH_3COO)$	672	467	3	1401	–
Glutamic acid	556.5	387	6 7	2322 2709	O–H in carboxyl group
Citric acid	405	282	6	1692	1700 ν (C=O) by sat, carboxylic acid 3000 OH of carboxylic group in H bond 3500–3550 OH in carboxylic group
Nifedipine	507.6	353	3 4 5	1056 1408 1760	1250–1300 esters of aromatic acids 1580–1650 C=C and C–H stretching 1370–1385 (C–CH_3) ν_s; 1435–1470 (C–CH_3) ν_{as}
Acetylsalicylic acid	389.7	271	4 5 6	1084 1355 1626	1230–1250 acetates 1680–1700 C=O stretching in acyl acid 1770–1800 esters with phenyl group

lyze the thermal 'sensitive' part of a molecule, by means of an adequate processing of the thermogravimetric data, in connection with the IR spectra.

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