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THERMAL STABILITY OF FOOD ADDITIVES OF GLUTAMATE AND BENZOATE TYPE

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Many years ago, thermal analysis earned its place as a current instrumentation technique in assisting/solving the analytical problems of pharmaceuticals. A relative new trend is the study of the thermal stability of food additives in connection with the molecular structure.

The studied compounds were: natrium and potassium glutamate, respectively natrium, potassium and calcium benzoate.

The thermogravimetric data (TG) were obtained in dynamic nitrogen atmosphere, with open Pt crucible and heating rates of 5, 7, 10 and 12 K min^{-1}, using a Perkin-Elmer TGA7 equipment.

In order to estimate the non-isothermal kinetic parameters, the Friedman's differential-isoconversional method and the method suggested by Budrugeac and Segal (based on the compensation effect) were used.

A variation of the activation energy *vs*. conversion was observed by using Friedman's method. The discrimination between the different reaction steps was performed by the non-parametric kinetic method, suggested by Sempere, Nomen and Serra. This is due to a complex process.

The thermal stability data are very important for avoiding a possible misuse by processing of the studied food additives.

Keywords: *compensation effect, food additives, isoconversional methods, non-isothermal kinetics, non-parametric kinetics (NPK)*

Introduction

The thermal analysis under non-isothermal conditions became a current instrumentation technique for food additives [1], also in connection with food processing. In an earlier paper [2] we report on the cyclodimerization of glutamic acid to diketopiperazine already at 210°C.

In the present paper we extend the study on thermal behavior of alkaline glutamates, largely used as taste fortifier and flavour enhancer. In addition, some alkaline and alkaline-earth benzoates, used as preservative additives, were studied.

Experimental

Reagent grade of monosodium (MSG) and monopotassium (MPG) glutamate, respective sodium (SB), potassium (PB) and calcium (CB) benzoate were used.

The thermogravimetric (TG) and derivate thermogravimetric curves (DTG) were obtained with a Perkin-Elmer TGA7 Thermobalance, in dynamic nitrogen atmosphere, at heating rates of 5, 7, 10 and 12 K min^{-1}.

Results and discussion

Examples of typical thermoanalytical curves are presented in Fig. 1.

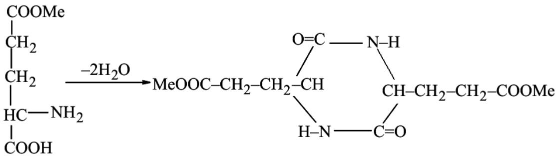
For all compounds the mass loss below 100°C is not discussed (humidity).

The alkaline glutamates exhibits different thermal behavior. MSG presents not well-separated steps between 150 and 245°C (even at low heating rates), whereas MPG presents a clear step of mass loss with a maximum of DTG at 185°C.

The benzoates also have different behavior: SB a single, well-defined step (max. at approx. 550°C), PB-two steps separated by 250°C and CB two rather superposed steps at relatively low temperatures.

The relative mass losses Δm_d determined from TG curves are systematized in Table 1, together with the calculated Δm_c for a suggested decomposition process.

For the glutamates we suggest a cyclodimerization similar with that for glutamic acid [2], with the loss of two water molecules (*Me*=Na or K reaction A).



Reaction A

According to the data in Table 1, in case of MSG, the Δm_c value agrees with the sum of Δm_d for the steps I and II. We should be trying to explain this

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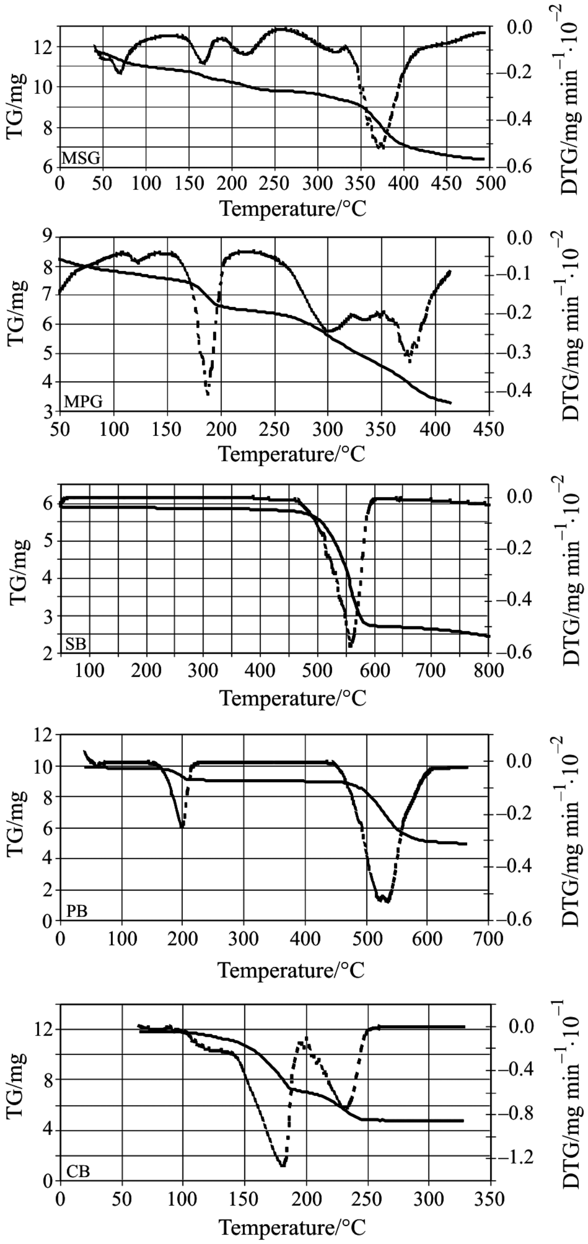

Fig. 1 TG and DTG curves at heating rate of 10 K min^{-1} for the studied compounds

by a kinetic analysis. By MPG the agreement between Δm_d and Δm_c is fulfilled and certain further decomposition take place at the end of the cyclodimerization.

For the benzoates, the suggested process is the decomposition in the ketone and carbonate (reaction B):

$$2C_6H_5\text{–}COOMe \rightarrow C_6H_5\text{–}CO\text{–}C_6H_5 + Me_2CO_3$$

Reaction B

By SB the process is clearly observed on the TG curves, but it is incomplete ($\Delta m_d < \Delta m_c$). In the case of PB the assignment is a little difficult. The sum of Δm_d for steps I and II agree rather good with the entire process (**B**), but the difference of 250°C between these steps is probably explainable due to a drastic change of the mechanism. The same observation is valid for CB with the mentions that the calcium salt is less stable in comparison with especially SB and that the steps I and II are rather superposed, not well-separated.

The existence of two TG steps under non-isothermal conditions for reaction generally accepted and known in organic chemistry make it necessary to investigate some kinetic and mechanistic aspects of these reactions.

Kinetic analysis

Following the recommendations of the 'ICTAC 2000 Project' [3], we begin with the Friedman's differential-isoconversional method [4], using the equation:

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \ln[Af(\alpha)] - \frac{E}{RT} \qquad (1)$$

where α is the conversion degree, β – heating rate, A – the preexponential factor and E – the activation energy in sense of Arrhenius equation.

From the data presented in Table 2, it results a significant dependence of the activation energy on the degree of conversion. Therefore, the method of Budrugeac and Segal [5–7] was applied. This method considers a dependence of the activation energy on the degree of conversion described by:

$$E=E_0+E_1\ln(1-\alpha) \qquad (2)$$

and a compensation effect described by:

$$\ln A=aE+b \qquad (3)$$

with the general equation:

$$\ln\left(\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}\right) = \left(b + aE_0 - \frac{E_0}{RT}\right) + \left(aE_1 - \frac{E_1}{RT} + n\right)\ln(1-\alpha) \qquad (4)$$

The parameters E_0, E_1, a, b and n were obtained and systematized in Table 3. The low values of E_0 by CB account for its lower thermal stability. Also it is noticeable the identical value of E_0 for MSG and MPG.

In order to obtain supplementary information on the reactions mechanism, the non-parametric kinetic (NPK) method, recently modified by the authors [8–10], was used. This method regards the reaction rate as a surface in three dimensional space were the axis are the degree of conversion (α), the temperature (T) and the rate of the degree of conversion ($\mathrm{d}\alpha/\mathrm{d}t$ or $\beta(\mathrm{d}\alpha/\mathrm{d}T)$). This surface can be discretized

Table 1 Determined and calculated mass loss of the decomposition step

Compound	Step	Mass loss, Δm_d/%, at different heating rate/K min^{-1}				Calculated mass loss, Δm_c/%
		5	7	10	12	
MSG	I II	4.1 4.5	4.0 5.0	4.1 5.0	4.5 5.5	I+II 10.6
MPG	I	11.4	11.2	11.6	11.5	9.7
SB	I	52.3	51.0	52.7	53.1	63.0
PB	I II	7.4 45.4	7.8 41.0	7.4 43.2	8.0 39.5	I+II 56.8
CB	I II	36.6 30.2	38.0 30.4	36.3 30.3	35.6 31.5	I+II 64.5

Table 2 Activation energy (kJ mol^{-1}) obtained with the Friedman's differential-isoconversional method

Sample	Step	α								
		0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
MSG	I II	166.3 240.8	232.1 203.9	225.8 192.9	234.4 169.6	242.8 149.9	216.1 191.3	183.5 191.4	188.8 158.3	195.5 152.6
MPG	I	199.3	237.6	233.8	110.1	175.6	158.2	165.6	183.7	60.4
SB	I	256.9	260.0	206.8	281.0	316.7	364.0	386.0	415.8	428.1
PB	I II	72.5 291.2	65.3 332.4	59.3 312.4	55.8 329.2	52.8 332.0	51.6 318.2	50.9 224.6	52.8 166.5	45.7 88.98
CB	I II	73.7 52.1	64.1 49.5	55.9 58.9	62.2 52.9	63.0 53.0	66.3 52.2	70.2 52.3	61.5 52.6	107.8 59.2

Table 3 Kinetic parameters according with Eq. (4)

Sample	Step	E_0/kJ mol^{-1} (Eq. (8))	E_1/kJ mol^{-1} (Eq. (8))	$a\cdot 10^4$/mol J^{-1} (Eq. (7))	b (Eq. (7))	n	Corr. coeff.
MSG	I II	222.8 210.5	17.9 33.0	2.77 2.54	–5.06 –6.17	1.5 1.8	0.99992 0.99961
MPG	I	222.7	38.6	2.63	–4.86	1	0.99997
SB	I	236.9	–98.9	1.48	–6.19	1.4	0.99999
PB	I II	64.6 363.7	9.4 110.9	2.29 1.44	–4.27 –3.53	0.4 2	0.99905 0.9998
CB	I II	56.65 51.9	–14.5 –1.98	2.64 2.31	–5.3 –5.17	0.3 0.2	0.99969 0.974

and organized in an $i \times j$ matrix A, where the column account for the temperature T_j and the rows refer to the degrees of conversion α_i, i.e.

$$A = g(\alpha_i) f(T_j) \tag{5}$$

The NPK method uses the singular value decomposition algorithm to decompose matrix A:

$$\mathrm{A} = \mathrm{U}(\mathrm{diag}\ s)\mathrm{V}^{\mathrm{T}} \tag{6}$$

The vector u_1 given by the first column of the matrix U is analyzed *vs*. α (to determine the kinetic model) and the vector v_1, the first column of the matrix V, is analyzed *vs*. T (to determine the Arrhenius parameters).

The Arrhenius equation was applied for $f(T)$ and the Šesták–Berggren equation [11] for the effect of the conversion degree:

$$g(\alpha) = \alpha^{\mathrm{m}}(1-\alpha)^{\mathrm{n}} \tag{7}$$

If the vector s has two significant values s_1 and s_2, there are two elementary processes and the discrimination between them depends on the values of the corresponding explained variance λ_1 and λ_2.

The results of this treatment of the TG data are systematized in Tables 4 and 5. With two exceptions all the secondary processes are less significant ($\lambda_2 < 10\%$).

For understanding this process of the decomposition steps, it is useful to compare the values of the m and n parameters of Eq. (7).

Table 4 Kinetic parameters for the preponderant process

Sample	Step	λ/%	E/kJ mol^{-1}	A/min^{-1}	n	m
MSG	I	73.12	114.0	$1.15\cdot10^{13}$	2	–
	II	88.53	115.4	$6.35\cdot10^{11}$	2	–
MPG	I	81.9	127.9	$9.14\cdot10^{13}$	1	–
SB	I	73.2	174	$4.3\cdot10^{10}$	3/2	1
PB	I	81.6	65.03	$5.66\cdot10^{6}$	1	1
	II	94.4	215.3	$3.51\cdot10^{13}$	3/2	–
CB	I	83.2	77.3	$4.48\cdot10^{8}$	3/2	1
	II	88.3	44.6	$1.66\cdot10^{4}$	1	1

Table 5 Kinetic parameters for the secondary process

Sample	Step	λ/%	E/kJ mol^{-1}	A/min^{-1}	n	m
MSG	I	23.96	255.2	$1.47\cdot10^{29}$	1/3	–
	II	9.09	536.3	$5.28\cdot10^{55}$	3/2	–
MPG	I	17.6	273.6	$1.91\cdot10^{32}$	–	1
SB	I	26.4	764	$2.6\cdot10^{47}$	–	3
PB	I	17.2	238	$3.09\cdot10^{25}$	–	3
	II	5.4	67.7	$2.65\cdot10^{42}$	1	3/2
CB	I	16.7	238	$5.62\cdot10^{26}$	–	3
	II	11	301.3	$3.07\cdot10^{30}$	–	3

By MSG, the practically identical values of the activation energy argued for two strong superposed steps with the same second order reaction in respect of (1–α). For MPG and MSG the E values are approximately the same, but the kinetic in respect of (1–α) is of first order.

By the benzoate salts the values of E lay in a large range, and the $m\neq0$ indicate a contribution of the nucleation process on the kinetic law.

Conclusions

- By the thermal decomposition of food additives of glutamate and benzoate type, some toxic compounds like diketopiperazine and diphenyl-ketones appear. Because all the decomposition steps proceed already at 150°C, the thermal stability data should determine a serious restriction of the upper limit of the temperature by food processing.
- For the kinetic analysis, these mentioned first steps of the decomposition are of importance. From the three utilized methods, only the NPK is able to offer a less speculative manner of discussions on decomposition process.
- By the glutamic salts the kinetic is near a first order or second order homogeneous reaction; by the benzoates, the contribution of a nucleation process is observed.

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