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THERMAL DECOMPOSITION OF SOME CHEMICAL COMPOUNDS USED AS FOOD PRESERVATIVES AND KINETIC PARAMETERS OF THIS PROCESS

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Abstract

Thermal decomposition processes of selected chemicals used as food preservatives such as sodium formate, sodium propionate, sodium nitrates(V and III) and sodium sulphate(IV) were examined by the derivatographic method. Based on the curves obtained, the number of decomposition stages and characteristic temperatures of these compounds have been found. Mass decrements calculated from TG curves ranged from 28.9% for sodium formate to 77.8% for sodium nitrate(V), while sodium sulphate showed a mass increment of 5.6%. Kinetic parameters such as activation energy (E_a), frequency factor (A) and reaction order (n) were calculated from TG, DTG and T curves. Sodium formate shows the highest values of E_a and A which amount to 171.7 kJ mol^{-1} and $5.8 \cdot 10^{14}$ s^{-1}, respectively, while the lowest ones, E_a=28.2 kJ mol^{-1} and A=$3.65 \cdot 10^2$ s^{-1} belong to sodium nitrate(V).

Keywords: food preservatives, kinetic parameters, thermal decomposition

Introduction

Food preservatives are chemicals that prevent food from decaying, prolonging food life with relatively low doses not exceeding 0.2% and sometimes even considerably lower. They show no or almost no effects on the flavour of food being preserved [1]. Food preservatives function is either to kill microorganisms or inhibit their growth, which prevents undesirable processes such as fermentation, mildew growing or rotting. However, not all antiseptics may be used in food due to their toxicity. There are only ten various chemicals permissible as food preservatives in Poland [2], such as:

1. Benzoic acid (E 210) and sodium benzoate (E 211);
2. *p*-Hydroxybenzoic acid ethyl ester (E 214) and *p*-hydroxybenzoic acid ethyl ester sodium salt (E 215);
3. *p*-Hydroxybenzoic acid propyl ester (E 216) and *p*-hydroxybenzoic acid propyl ester sodium salt (E 217);
4. Formic acid (E 236), sodium formate (E 237) and calcium formate (E 238);
5. Nisin (E 234);
6. Propionic acid (E 280), sodium propionate (E 281) and calcium propionate (E 262);

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7. Sodium sulphate (IV) (E 221);
8. Sodium sorbate (E 201);
9. Sodium nitrate (V) (E 251), potassium nitrate (V) (E 252);
10. Sodium nitrate (III) (E 250).

Among them, compounds such as sodium sulphate (IV), sodium sorbate and sodium benzoate have found the most common use.

Aim of the present study was to examine the thermal decomposition of selected food preservatives at high temperatures and to determine the kinetic parameters of these processes.

Materials and methods

Following compounds were used for the study: sodium benzoate (POCh S. A. – Gliwice), sodium propionate (Fluka), sodium formate (Fluka), sodium nitrate (V, III) and sodium sulphate (IV) (POCh S. A. – Gliwice).

Thermal curves were recorded by means of a Paulik-Paulik-Erdey 1000/1500 Derivatograph of MOM (Hungary). Weighed portions of the sample under investigation were from 200 to 600 mg depending on the density. Samples were heated up to 1273 K under static atmosphere of air a rate of 10 deg min^{-1} in corundum crucibles, using α-Al_2O_3 as reference.

Based on the TG, DTG and T curves obtained, the following kinetic parameters of first step thermal decomposition were determined: activation energy (E_a), frequency factor (A) and reaction order (n). The values of the kinetic parameters are one of the most important characteristics in thermal analysis. In accurate determine conditions experiment the values of the kinetic parameters are characteristic for particular chemicals [3]. The calculations were carried out, assuming that deviations from the Arrhenius equation can be correlated linearly only in the initial phase decomposition of the examined samples [4–7].

The Arrhenius equation in logarithmic form (Eq. (1)) was solved graphically:

$$\log(\mathrm{d}m/\mathrm{d}t)=\log A+n\log c-E_a/R\mathrm{T} \quad (1)$$

The value of c was calculated from Eq. (2)

$$c=(\Delta m_\infty-\Delta m)/\Delta m_\infty \quad (2)$$

where Δm_∞ – maximum mass loss at the given stape. In order to calculate the activation energy E_a, the plot function $\log(\mathrm{d}m/\mathrm{d}t)=f(1/T)$ was made as shown in Fig. 1. Knowing the value of E_a, function (Eq. (3)) was plotted:

$$1/T(\mathrm{tg}\alpha)+\log(\mathrm{d}m/\mathrm{d}t)=f(\log c) \quad (3)$$

as shown in Fig. 2. The slope of the straight line obtained corresponds to the order of reaction n (n=tgβ). The value pointed out by the straight line on the axis of ordinates is equal to log$A$.

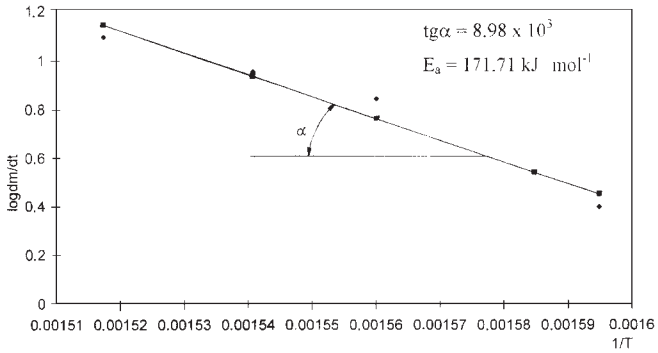

Fig. 1 Graphic dependence log(dm/dt)=f(1/T) applied for appointing activation energy E_a of I step thermal decomposition sodium formate

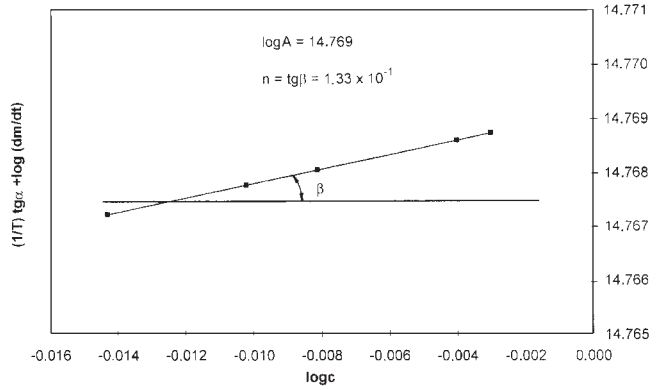

Fig. 2 Graphic dependence log(dm/dt)+1/T log$a$=f(log$c$) applied for appointing frequency factor (A) and reaction order (n) of I step thermal decomposition sodium formate

Results and discussion

Figure 3 shows groups of derivatographic curves obtained for sodium formate (Fig. 3a), sodium benzoate (Fig. 3b) and sodium propionate (Fig. 3c).

Sodium formate HCOONa

From the course of the TG, DTG and DTA curves (Fig. 3a) it can be seen that HCOONa is decomposed in three stages. The decomposition begins at a temperature of 510 K, melting of sample endothermic peak in the DTA curve without mass decrement. The first stage of decomposition takes place in the temperature range 543–733, most rapidly at 703 K. The mass decrement at this stage is 10.7%. In this temperature range the DTA curve indicates an endothermic reaction (700 K) which suddenly turns

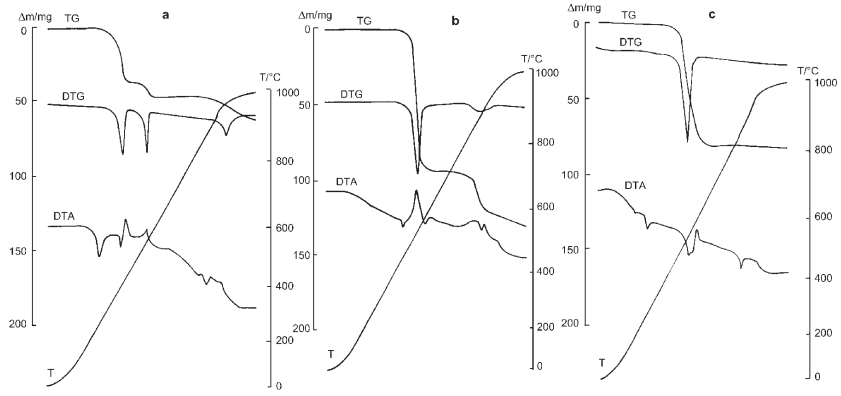

Fig. 3 Thermal curves of samples: a – sodium formate m_0=0.200 g, TG=200; b – sodium benzoate m_0=0.200 g, TG=200; c – sodium propionate m_0=0.208 g, TG=200

to an exothermic one at 720 K. The second decomposition stage proceeds the most rapidly at 843 K, with mass decrement being 5.6%. The small exothermic peak in the DTA curve corresponds to the second stage. The small endothermic peak in the DTA curve appears at a temperature 1123 K it is the melting point Na_2CO_3 formed in the crucible. The thermal decomposition of sodium formate is a complex process . Based on the TG, DTG, DTA curves and earlier studies [8–10] the following reactions are possible:

I stage

$$2HCOONa \xrightarrow{543-733\ K} (COONa)_2 + H_2(\uparrow) \quad (4)$$

$$2HCOONa \xrightarrow{543-733\ K} Na_2CO_3 + CO(\uparrow) + H_2(\uparrow) \quad (5)$$

II stage

$$(COONa)_2 \xrightarrow{733-848\ K} Na_2CO_3 + CO(\uparrow) \quad (6)$$

III stage

$$Na_2CO_3 \xrightarrow{above\ 923\ K} Na_2O + CO_2(\uparrow) \quad (7)$$

Sodium benzoate C_6H_5COONa

Figure 3b shows derivatographic curves obtained for sodium benzoate. Thermal decomposition C_6H_5COONa takes place in two stages. It begins at a temperature of 728 K melting of the sample (endotermic peak in the DTA curve). The first stage of thermal decomposition takes place at 783 K (peak in the DTG curve). Mass decrement at this stage is 35.8%. The second mass loss observed at 1103 K, it is smaller than the first – 12.3% of its mass. By reaching the temperature 1153 K a small endothermic peak appears in the DTA curve the melting point Na_2CO_3. Total mass decrement of the sodium benzoate sample on heating within the temperature range from 293 to 1273 K amounts to 48.1%. Based on derivatographic curves and earlier ther-

mal analyses [11–12] decomposition of sodium benzoate involves the following non-stoichiometric reactions:

I stage $$C_6H_5COONa \xrightarrow{748-848\ K} Na_2CO_3 + H_2(\uparrow) + CO(\uparrow) \quad (8)$$

II stage $$Na_2CO_3 \xrightarrow{above\ 948\ K} Na_2O + CO_2(\uparrow) \quad (9)$$

Sodium propionate C_2H_5COONa

The thermal analysis curves of this compound are shown in Fig. 3c. The first endothermic peak in the DTA curve at temperature 553 K corresponds to the melting of the sample. The first decomposition stage, between 673 and 843 K is endothermic. The mass loss 31.7% corresponds to the loss of H_2O and CO. In the final stage temperature after melting Na_2CO_3 (endothermic peak DTA in 1123 K); partially conversion Na_2CO_3 to Na_2O. Based on the derivatographic curves [13] the following reactions are possible:

I stage $$2CH_3CH_2COONa \xrightarrow{673-843\ K} Na_2CO_3 + 4H_2O + 5CO(\uparrow) \quad (10)$$

$$\overset{+4\ 0}{\underset{2}{}}$$

II stage $$Na_2CO_3 \xrightarrow{above\ 970\ K} Na_2O + CO_2(\uparrow) \quad (11)$$

Figure 4 shows groups of derivatographic curves obtained for sodium nitrate (V) (Fig. 4a), sodium nitrate (III) (Fig. 4b) and sodium sulphate (IV) (Fig. 4c).

Sodium nitrate (V) $NaNO_3$

The compound is thermally decomposed within one stage (Fig. 4a). The decomposition begins at a temperature of 593 K melting of sample (endothermic peak in the DTA curves) without mass decrement. Thermal decomposition in the temperature

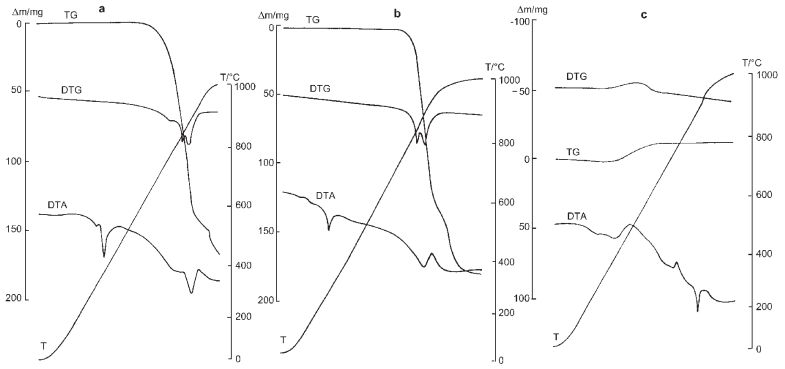

Fig. 4 Thermal curves of samples: a – sodium nitrate(V) m_0=0.200 g, TG=200; b – sodium nitrate(III) m_0=0.200 g, TG=200; c – sodium sulphate(IV) m_0=0.200 g, TG=200

Table 1 Date based on thermoanalytical curves of thermal decomposition process of food preservatives

Name of compounds	I stage				II stage				III stage				All mass loss/%
	T_i/K	T_m/K	T_f/K	Δm_I /%	T_i/K	T_m/K	T_f/K	Δm_{II}/%	T_i/K	T_m/K	T_f/K	Δm_{III}/%	
HCOONa	543	703	733	10.7	733	843	848	5.6	923	1173	–	12.6	28.9
C_6H_5COONa	748	783	848	35.8	948	1103	1253	12.3	–	–	–	–	48.1
CH_3CH_2COONa	673	783	843	31.7	–	–	–	14.6	–	–	–	–	46.3
$NaNO_3$	793	11.43	1243	77.8	–	–	–	–	–	–	–	–	77.8
$NaNO_2$	963	1173	1263	73.3	–	–	–	–	–	–	–	–	73.3
Na_2SO_3	573	773	823	–5.6	–	–	–	–	–	–	–	–	–5.6

T_i – initial temperature
T_m – peak temperature
T_f – final temperature

range 793–1243 K corresponds to the loss of NO. By reaching the final measurement temperature 1273 K, the samples loses 77.8%. Thermal decomposition $NaNO_3$ according to the following reaction [14–15]:

$$2NaNO_3 \xrightarrow{793\text{–}1243\ K} Na_2O+2NO(\uparrow)+1.5O_2(\uparrow) \quad (12)$$

Sodium nitrate (III) $NaNO_2$

The decomposition processes of $NaNO_2$ and $NaNO_3$ are similar (Fig. 4b) within one stage. It starts with melting at a temperature 553 K (endothermic peak DTA). Mass decrement of the sample begins at 963, proceeds violently at 1173 and is terminated at 1243 K. For $NaNO_2$ the decomposition temperatures are slightly lower than for $NaNO_3$, with its mass decrement amounting to 73.3%.

The DTA curve indicates an endothermic reaction (970 K) which suddenly turns to an exothermic one at 1200 K. While decomposition $NaNO_2$ the following reaction is possible:

$$2NaNO_2 \xrightarrow{973\text{–}1243\ K} Na_2O+2NO(\uparrow)+0.5O_2(\uparrow) \quad (13)$$

Sodium sulphate (IV) Na_2SO_3

Figure 4c shows the thermoanalytical curves obtained for Na_2SO_3. A different behaviour was observed during the heating Na_2SO_3 at 773 K which shows a gain in mass by 5.6%. This is due to the oxidation of Na_2SO_3 to Na_2SO_4 with air oxygen at elevated temperature. The following reaction is possible [16–17]

$$Na_2SO_3 \xrightarrow{573\text{–}823\ K} Na_2SO_4 \quad (14)$$

The values of characteristic temperatures and mass decrements for all investigation compounds are given in Table 1.

Kinetic parameters of the first stage of the examined compounds decomposition were calculated for the initial phase of that stage where the function $\log(dm/dt)= f(1/T)$ is a straight line. The kinetic parameter values found for the compounds examined are listed in Table 2.

Table 2 Kinetic parameters of I stage thermal decomposition some food preservatives

Name of compound	Kinetic parameters		
	Activation energy E_a/kJ mol^{-1}	Frequently factor A / s^{-1}	Order of reaction n
HCOONa	171.7	$5.88\cdot10^{14}$	$1.33\cdot10^{-1}$
C_6H_5COONa	161.2	$1.22\cdot10^{12}$	$1.92\cdot10^{-1}$
CH_3CH_2COONa	58.8	$7.97\cdot10^{4}$	$4.90\cdot10^{-1}$
$NaNO_3$	28.2	$3.65\cdot10^{2}$	$6.68\cdot10^{-1}$
$NaNO_2$	52.0	$5.64\cdot10^{4}$	$3.20\cdot10^{-1}$

The value of E_a for sodium formate HCOONa is 171 kJ mol^{-1}, the frequency factor A=5.88·10^{14} s^{-1}, and the reaction order n=1.33·10^{-1}. The kinetic parameters for sodium benzoate show lower values, namely: E_a=161 kJ mol^{-1}, A=1.22·10^{12} s^{-1} and n=1.92·10^{-1}. Sodium nitrate(V) shows the lowest activation energy E_a=28 kJ mol^{-1}, with its A and n values amounting to 3.65·10^{12} s^{-1} and 6.68·10^{-1}, respectively. The kinetic parameters for the remaining compounds under investigation assume intermediate values as listed in Table 2.

Conclusions

The compounds used as preservatives in food industry are of very different chemical character and therefore their thermal decomposition proceeds differently. Among six examined food preservatives in this study, only sodium formate HCOONa decomposes in three stages, its decomposition begins at the lowest temperature and it loses the least of its mass. The decomposition of sodium nitrate(III) $NaNO_2$ begins at the highest temperature, which indicates that it has the highest thermal stability among the examined food preservatives. The highest mass decrement due to thermal decomposition is shown by sodium nitrate(V).

The results obtained indicate that the derivatographic method may be used to examine the thermal decomposition of food preservatives. This method allows one to monitor the processes taking place on increasing the temperature of samples under testing.

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