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Short Communication

THE THERMAL STABILITY OF TWO SUBSTITUTED THIOAMIDES

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A derivatographic investigation was performed on the thermal behaviour of three thioamides and the nonisothermal kinetic parameters for the liquid-phase decomposition of N-acetylthiobenzamide were determined.

Thioamides substituted by an acyl group are characterized by high chemical and biological reactivities. Thus, a knowledge of the thermal stabilities of such compounds provides useful information concerning their stockage and handling conditions.

Following our earlier research on the thermal stability of thioamides [1], this paper deals with a thermal investigation of some N-acylthioamides.

Experimental

The following powdered compounds, synthesized and analysed according to methods described elsewhere [2, 3], were used: N-acetylthiobenzamide, N-benzoylthiobenzamide, thiobenzamide.

The heating curves were recorded with a Paulik–Paulik–Erdei Q–1500 derivatograph (MOM, Budapest) in static air atmosphere at various heating rates between 1.25 deg/min and 10 deg/min.

A Philips PW/1140 diffractometer was used to record the X-ray diffractograms of the solid powder. The diffractograms were recorded by using chromium K_α radiation.

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To determine the nonisothermal kinetic parameters of the thermal decompositions from the thermogravimetric data, three methods were applied: those of Coats and Redfern [4], Ozawa [5] and Freeman and Carroll [6]. The data were processed automatically with a TI 66 programmable computer.

Results and discussion

Figure 1 shows the thermal curves of N-acetylthiobenzamide recorded at 5 deg/min.

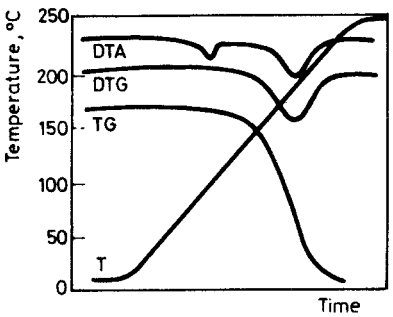

Fig. 1 The derivatogram of N-acethylthiobenzamide

The compound undergoes melting at 105° and then decompose in the temperature interval 113–203°. The temperature corresponding to the maximum decomposition rate (as shown by the TG and DTG curves) is 175°.

Table 1 gives the same data for the investigated compounds.

The last column in Table 1 contains the interplanar distances (*d*) corresponding to the most intense line in the X-ray powder diffractograms.

Table 1 Thermal stability and diffractometric data on the investigated compounds

Compound	Melting temperature, °C	Decomposition temperature interval	*d*, Å
N-acetylthiobenzamide	105	113–203	5.98
N-benzoylthiobenzamide	117	125–365	7.20
Thiobenzamide	115	120–300	3.80

Table 2 lists the values of the nonisothermal kinetic parameters for the liquid-phase decomposition of N-acetylthiobenzamide estimated with the above three methods.

Table 2 Values of nonisothermal kinetic parameters for liquid-phase decomposition of N-acetylthiobenzamide

Method												
Coats–Redfern						Ozawa			Freeman–Carroll			
n	β, deg/min	E, kcal/mol	E^*, kcal/mol	A, s^{-1}	K_{158}, s^{-1}	α	E, kcal/mol	E^*, kcal/mol	n	β, deg/min	E, kcal/mol	E^*, kcal/mol
1	5	27	26.66	$6.3 \cdot 10^{10}$	$1.5 \cdot 10^{-3}$	0.1	25		0.91	5	23	
	2.5	26		$3.15 \cdot 10^{10}$	$1.6 \cdot 10^{-3}$	0.3	24	25				24.5
	1.25	27		$1.2 \cdot 10^{11}$	$1.8 \cdot 10^{-3}$	0.4	25		0.99	2.5	26	
						0.5	26					
						0.6	25					
						0.7	25					
						0.8	25					

E^* – means average value of E

A quite satisfactory agreement between the values of the apparent activation energy can be observed.

Values of the "reaction order" $n = 1$ were obtained with the methods of Coats and Redfern and Freeman and Carroll. As far as the values of the preexponential coefficient are concerned, differences up to two orders of magnitude may be observed from the value predicted by transition state theory [7], according to which $A = 6 \cdot 10^{12}\ s^{-1}$ for $n = 1$.

The best agreement was obtained at 1.25 deg/min. The values of the rate constants at 158° for the three heating rates used, are also in quite satisfactory agreement.

From the constancy of the Ozawa plot slope for values of the conversion degree under the condition $0.1 < \alpha < 0.9$, a unique decomposition mechanism may be concluded.

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