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ON THE THERMAL STABILITY OF SOME THIOAMIDES

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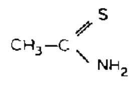
ABSTRACT

This paper presents some results concerning the thermal behaviour of thioacetamide, thiobenzamide and thiocinamamide. Some correlations between the previous thermal treatment, crystallinity and non-isothermal kinetic parameters of the thermal decomposition are discussed.

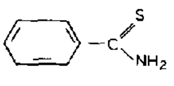
INTRODUCTION

The thermal decomposition of organic solids has been investigated to a lesser extent than that of organic solids. Among the reasons for this, one can mention: the complexity of such processes, which are often accompanied by melting or even sublimation; the variety of solid, liquid and gaseous products, etc. Unlike the decomposition of inorganic solids the localized beginning in some particular points of the crystal surface is questionable [1].

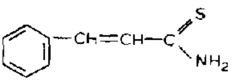
This paper deals with the thermal stability of thioacetamide, thiobenzamide and thiocinamamide. As it will be shown later, the above statements are entirely valid for the thermal behaviour of such compounds.



Thioacetamide



Thiobenzamide



Thiocinamide

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EXPERIMENTAL

Powders of thioacetamide, thiobenzamide and thiocinamamide, synthesized, purified and analysed according to methods described elsewhere, were used [2].

To gain information about the changes in crystallinity due to the thermal treatment and to determine the mean crystallite sizes, a Philips X-ray diffractometer (P.W. 1140/90) with chromium K_α radiation was used.

The heating curves were recorded using a Paulik–Paulik–Erdey type derivatograph (MOM, Budapest). Linear programs of heating, with heating rates varying from 1.2 to 10 K min^{-1}, were applied. For the non-isothermal kinetic study, to prevent mass and heat-transfer limitations, small amounts of powder (< 0.1 g) were used. To determine the non-isothermal kinetic parameters the integral method of Coats and Redfern [3] was used.

RESULTS AND DISCUSSION

Mean crystallite sizes

In Table 1 the mean crystallite sizes, $\bar{r}$, of the original recrystallized powders and those treated by melting and subsequent cooling, evaluated with Scherrer's formula [4], are given.

TABLE 1

Mean crystallite sizes of the original and treated powders

Compound and treatment	d (A) [a]	$\bar{r}$ (Å)
Thioacetamide: original, recrystallized from benzene (a)	3.58	311
Thioacetamide: heated until melting and subsequently cooled at ambient temperate on a watch glass (b)	3.58	415
Thioacetamide: treatment (b), but in a glass tube with thin walls (c)	3.58	311
Thiobenzamide: (a)	3.80	309
Thiobenzamide: (b)	3.80	413
Thiobenzamide: (c)	3.80	413
Thiocinamamide: (a)	5.02	303
Thiocinamamide: (b)	5.02	404
Thiocinamamide: (c)	5.02	amorphous

[a] Interplanar distance corresponding to the most intense X-ray diffraction line.

From these data an increase in the mean crystallite sizes with respect to the original material due to treatment (b) can be noted.

Crystallinity data

Information concerning the thermal behaviour of the investigated thioamides without chemical reaction can be obtained from the influence on the samples crystallinity of heating to the melting temperature and subsequently cooling to ambient temperature. As a measure of the crystallinity, the ratio of the intensities (corresponding to the most intense line from the X-ray diffractogram) after treatments (b) or (c) and (a) (Table 1) will be considered.

Thioacetamide

For treatment (b) (cooling the melt on a watch glass) the ratio of the intensities is 0.32, while for treatment (c) (cooling the melt in a glass tube with thin walls) this ratio is 0.60. Thus, in this case the crystallinity has a higher value for treatment (c). To account for these experimental facts one has to note that in the case of treatment (b), which consists of a surface cooling, the cooling rate is higher than in the case of treatment (c), cooling in the bulk. Under such consitions the surface fast-cooled material keeps, to great extent, the lack of long-range order characteristic of the molten state, and exhibits a lower value of crystallinity, as shown by experience.

Thiobenzamide

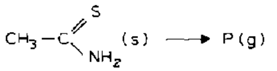
The intensity of the X-ray diffraction line corresponding to $d = 3.80$ Å (maximum intensity) does not change with heating up to the melting temperature and subsequent cooling, so we do not have significant changes in crystallinity to report due to the thermal treatment.

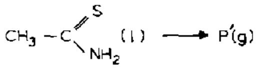
Thiocinamamide

Treatment (b) leads to a ratio of intensities for the line with $d = 5.12$ Å which equals 0.22 while treatment (c) leads to a material which has no crystallinity at all as shown by the diffractogram which does not exhibit any diffraction maximum. This inversion with respect to the thermal behaviour of thioacetamide can be assigned to the difference between the thermal conductivities of the two compounds. The thiocinamamide is probably characterized by a higher value of the thermal conductivity than the thioacetamide, thus the cooling of the system compound–glass is limited by the cooling rate of the glass. Under such conditions the glass tube with thin walls exhibits a higher cooling rate and the solidified material keeps a metastable amorphous structure.

The heating curves of the original thioacetamide recrystallized from benzene recorded in air at a heating rate of 10 K min^{-1} are given in Fig. 1.

On the DTA curve a first endothermic peak located at 110°C corresponds to the melting of the substance. On the same curve two more endothermic peaks are noted, a weak one located at 140°C and a strong one located at 165°C. The last two peaks can also be found on the DTG curve, slightly shifted to lower temperatures due to the thermal inertia of the differential termocouple. Actually, there is a certain overlap between the melting and first decomposition steps. This is perhaps the reason why the first decomposition step occurs mainly in the solid phase. As shown by the DTG curve (Fig. 1) the main decomposition (second decomposition step) occurs in the liquid phase. There was no solid residue in the crucible after the occurrence of the second decomposition step. Thus, the decomposition of the thioacetamide occurs in the following two steps





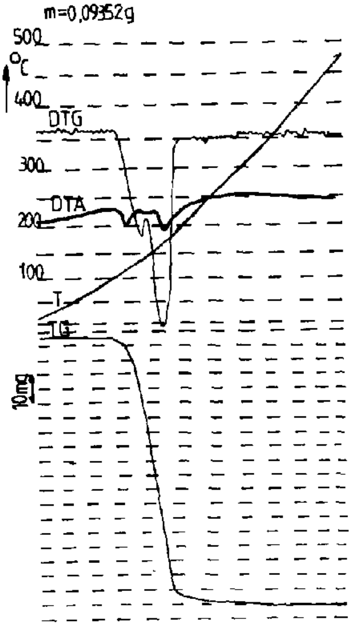


Fig. 1. The derivatogram of thioacetamide submitted to treatment (a).

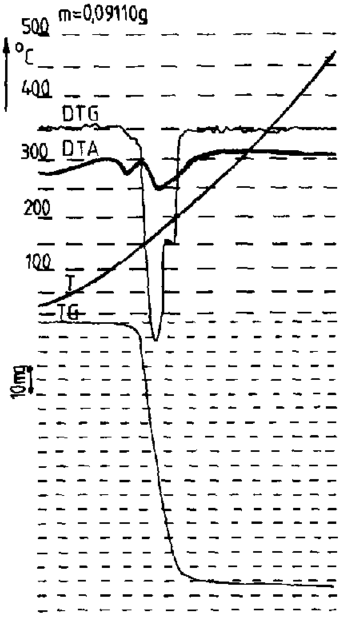


Fig. 2. The derivatogram of thioacetamide submitted to treatment (c) in air at $\beta = 10$ K min^{-1}.

TABLE 2

Non-isothermal kinetic parameters for the second decomposition step of thioacetamide

β (K min^{-1})	n	E (kcal mol^{-1})	A (s^{-1})
10	1	67	1.2×10^{32}
2.5	1	27.5	8.8×10^{12}

where P(g) and P′(g) represent gaseous products. This observation is valid for all the substances investigated in this work. Qualitatively the derivatogram corresponding to the thioacetamide submitted to treatment (b) does not exhibit any new changes with respect to those reported for the original recrystallized material. Treatment (c) induces some changes in the heating curves as shown in Fig. 2.

Inspection of this derivatogram shows that the main decomposition step occurs at quite the same temperature (162.5°C) as in the original material (treatment a), but a second decomposition step occurs at higher temperatures with the maximum rate at 190°C, maybe due to the thermal decomposition of some intermediate generated during the thermal treatment.

The non-isothermal kinetic parameters for the first step of decomposition of the original material at a heating rate, $\beta = 10$ K min^{-1} are: $n = 0$; $A = 1.8 \times 10^7$ s^{-1} *; $E = 19$ kcal mol^{-1}. The value 0 for the reaction order, n, is predicted by a general theoretical treatment for solid–gas decompositions [5] and by a particular model for the decomposition of organic solids with melting [1].

Concerning the second step of decomposition, as shown in Table 2, the kinetic parameters change with the heating rate indicating some heat transfer limitations.

Under such conditions the values of the kinetic parameters at 2.5 K min^{-1} should be considered to be close to the true ones. The value $n = 1$ is typical for kinetic-limited decompositions, the value of the pre-exponential factor being very close to that predicted by the transition state theory [6].

The heating curves of thiobenzamide, obtained in air at $\beta = 10$ K min^{-1}, are given in Fig. 3.

Inspection of this figure shows a close similarity between the thermal behaviour of thiobenzamide and that of thioacetamide. The endothermic effect corresponding to the melting is located at 120°C and partially overlaps the solid-state decomposition (first step) whose maximum rate is located at 180°C. As far as the main liquid-state decomposition is concerned its maximum decomposition rate is located at 230°C.

The values of the non-isothermal kinetic parameters for the solid-state decomposition (first step) at $\beta = 2.5$ K min^{-1} are: $n = 0$; $E = 30$ kcal

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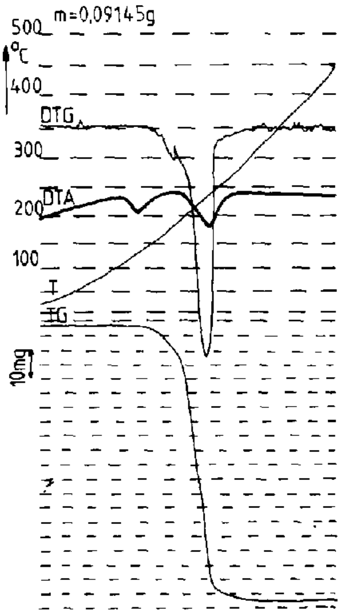
* The kinetic equation $d\alpha/dt = k$ was considered.

mol^{-1}; $A = 2 \times 10^{12}$ s^{-1}. As in the former case these values of the kinetic parameters are characteristic for a solid-state decomposition accompanied by melting.

For the liquid-state decomposition no changes in the kinetic parameters with the changes in the heating rate are to be reported. The values of the non-isothermal kinetic parameters for this second decomposition step are: $n = 1$; $E = 44$ kcal mol^{-1}; $A = 2.3 \times 10^{17}$ s^{-1}, as required by the decomposition of liquids according to a unimolecular mechanism.

The heating curves of the thiocinamamide recrystallized from benzene in air at $\beta = 10$ K min^{-1} are given in Fig. 4.

As shown by these curves the thermal behaviour of the thiocinamamide is quite similar to that of the other two thioamides already discussed. Thus, the melting can be noted as an endothermic peak located at 160°C on the derivatogram which overlaps the first solid-state decomposition step whose maximum rate is difficult to locate. The second decomposition step (liquid-state decomposition) occurs at higher temperatures with a maximum rate located at 250°C. The derivatogram of the thiocinamamide submitted to treatment (c) in air at $\beta = 10$ K min^{-1} (Fig. 5) does not exhibit the endothermic peak due to the melting, and decomposition takes place in a single step. This thermal behaviour is in total agreement with the previously mentioned crystallinity data.



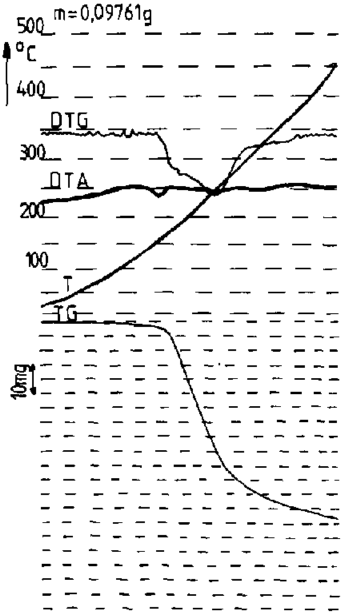


Fig. 3. The derivatogram of thiobenzamide submitted to treatment (a).

Fig. 4. The derivatogram of thiocinamamide submitted to treatment (a).

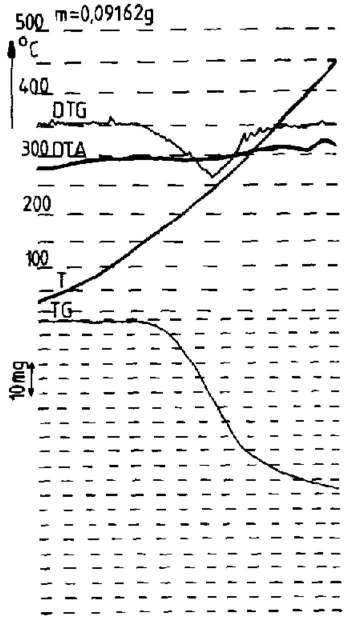


Fig. 5. The derivatogram of thiocinamamide submitted to treatment (c).

The coincidence of the temperatures corresponding to maximum decomposition rates for the crystallized thiocinamamide (Fig. 4, second peak) and for the treated amide suggests a transition between two isomeric forms in the crystallized material, induced by thermal treatment. The non-isothermal kinetic parameter values of the decomposition for the thiocinamamide submitted to treatment (a) at $\beta = 1.2$ K min^{-1} are: $n = 1$; $E = 23$ kcal mol^{-1}; $A = 4.5 \times 10^{6}$ s^{-1}. For the material submitted to treatment (c) these values change as follows: $n = 1$; $E = 23$ kcal mol^{-1}; $A = 4.4 \times 10^{10}$ s^{-1}. In this last case the value of the pre-exponential factor is closer to that theoretically predicted for unimolecular decompositions [6].

CONCLUSIONS

(1) The crystallinity of the thioamide solid samples depends on their previous thermal treatment.

(2) The thermal curves of the compounds are sensitive to their previous thermal treatment.

(3) The derivatograms of all the three thioamides investigated exhibit melting and two decomposition steps, namely solid and liquid-state decompositions.

(4) All the decompositions lead only to final gaseous products under the above conditions.

(5) Taking into account the temperatures corresponding to the maximum

decomposition rate (second decomposition peak) the investigated thioamides exhibit the following order of thermal stability: thioacetamide < thiobenzamide < thiocinamamide.

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