Thermochimica Acta, 87 (1985) 335–341
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ON THE THERMAL STABILITY OF SOME SUBSTITUTED THIOAMIDES

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(Received 14 November 1984)

ABSTRACT

The authors present some results concerning the thermal decomposition of some substituted thioamides.

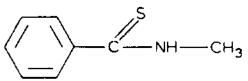
INTRODUCTION

In a previous paper our results concerning the thermal stability of thioamide, thiobenzamide and thiocinnamamide were presented [1]. Following these investigations this paper deals with the influence of substitution at the nitrogen atom and in the aromatic ring upon the thermal behaviour of thiobenzamide and thiocinnamamide.

EXPERIMENTAL

Powders of *N*-methylthiobenzamide (**1**), *N*,*N*-dimethylthiobenzamide (**2**), *N*-methylthiocinnamamide (**3**), *p*-methoxythiocinnamamide (**4**) and *p*-chlorothiocinnamamide (**5**) were synthesized, purified and analysed according to methods described elsewhere [2].

To gain information on the changes in crystallinity due to the thermal treatment and to determine the mean crystallite sizes a Philips X-ray diffractometer (PW 1450) with the $K\alpha$ radiation of chromium was used. The heating curves were recorded using a Paulik–Paulik–Erdey type MOM derivatograph (Budapest). A linear program of heating at a heating rate



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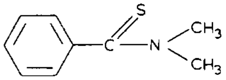

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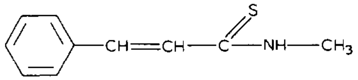

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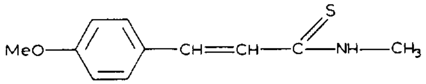

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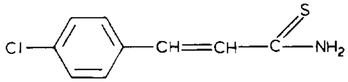

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$\beta = 10$ K min^{-1} was applied. For the non-isothermal kinetic study, to prevent mass and heat transfer limitations, small amounts of powder (< 0.1 g) were used. In order to evaluate the non-isothermal kinetic parameters the integral method of Coats and Redfern [3] was used.

TABLE 1

Mean crystallite sizes of the original (recrystallized) and treated powders

Compound and treatment	d (Å) [a]	$\bar{r}$ (Å)
N-Methylthiobenzamide recrystallized from benzene + petroleum ether	3.92	305
N-Methylthiobenzamide treated	3.92	406
N,*N*-Dimethylthiobenzamide recrystallized from benzene + petroleum ether	5.27	605
N,*N*-Dimethylthiobenzamide treated	5.27	619
N-Methylthiocinnamamide recrystallized from ethanol	4.17	614
N-Methylthiocinnamamide treated	4.17	625
p-Chlorothiocinnamamide recrystallized from ethanol	1.93	248
p-Methoxythiocinnamamide recrystallized from benzene	2.23	245

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

RESULTS AND DISCUSSIONS

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

As in the case of unsubstituted thioamides, there is a noticeable increase in the mean crystallite sizes with respect to the original material due to the thermal treatment (actually, the difference is significant only for *N*-methylthiobenzamide).

Crystallinity data

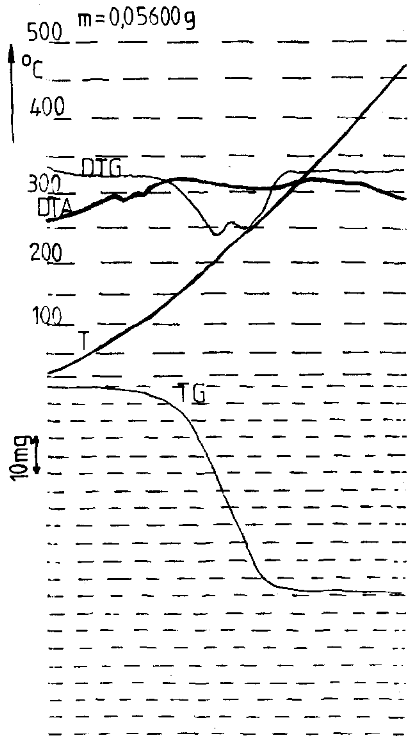
The values of the crystallinity were obtained in the same way as in a previous paper [1]. Generally, the thermal treatment, which consists in heating until melting and subsequent cooling at ambient temperature, leads to a decrease in the crystallinity, except for that of *N*-methylthiobenzamide which becomes higher after such a treatment. One can account for this abnormal behaviour of the *N*-methylthiobenzamide by assuming that the original material actually consists of a mixture of two species with different crystallinity values. The thermal treatment changes the less crystalline species into the high crystalline one.

Heating curves and non-isothermal kinetics

The heating curves of the original recrystallized *N*-methylthiobenzamide are given in Fig. 1. After two endothermic effects located at 84 and 116°C, which can be assigned to the melting of the two above-mentioned species, the derivatogram exhibits two decomposition steps located at 204 and 243°C, respectively. No residue was left in the crucible after decomposition had occurred. This observation is valid for all the total thermal changes investigated in this work. As far as the treated *N*-methylthiobenzamide is concerned, after melting, which occurs at 82°C as shown in Fig. 2, it exhibits a single decomposition step with the maximum rate located at 255°C.

The derivatographic data confirm the former assumption which was made to explain the crystallinity data. Indeed, the *N*-methylthiobenzamide obtained by thermal treatment exhibits a decomposition temperature quite close to that of the second maximum exhibited by the original material. This shows us that the second peak of the original material and the single peak of the treated material are due to the decomposition of the same compound.

The non-isothermal kinetic parameters for the decomposition of the original and treated materials are given in Table 2. Although the values of the reaction order, $n = 1$, is suitable for unimolecular liquid-state decompositions, only for step II is the value of the pre-exponential factor, A, close to that required by the transition state theory [5]. Thus, some physical



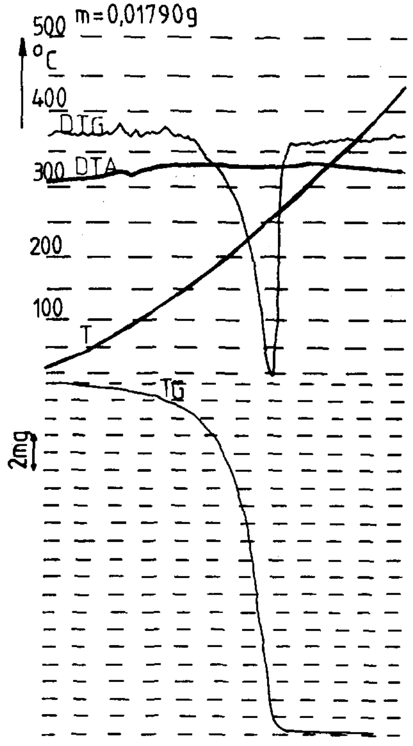


Fig. 1. Derivatogram of the original recrystallized *N*-methylthiobenzamide.

Fig. 2. The derivatogram of the treated *N*-methylthiobenzamide.

phenomena limiting the decomposition are suspected. This statement is confirmed by the relatively low values of the activation energy, *E*, for step I and for the decomposition of the treated material.

By comparing these results with those obtained for the thermal decomposition of thiobenzamide [1] one can conclude that the substitution induced noticeable changes in its thermal behaviour.

The heating curves for the original recrystallized *N*,*N*-dimethylthiobenzamide and that submitted to thermal treatment are given in Figs. 3 and 4, respectively. The derivatogram of the original material exhibits melting at 75°C and two decomposition steps which occur with maximum rates at 205 and 237°C. The derivatogram of the treated material looks quite similar, the three significant temperatures being 74, 194 and 233°C. The difference between the two TG and respective DTG curves is the extent of the decomposition steps. As in the former case the thermal treatment induces an extension of the second (high-temperature) decomposition step. Thus, in this case the original material and even the treated one behaved thermally as a mixture of two species in spite of the single melting temperature.

The non-isothermal kinetic parameters of the decomposition are given in Table 3. Taking into account the unusually high value of the pre-exponential factors (column 3 of Table 3), we suspected some apparent compensation

TABLE 2

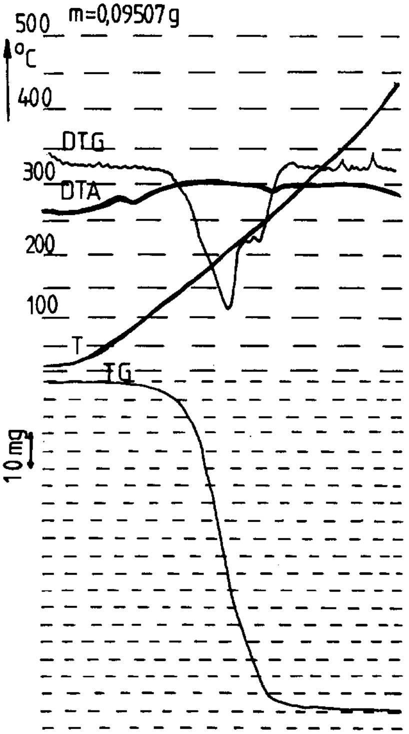
Non-isothermal kinetic parameters for *N*-methylthiobenzamide decomposition

Kinetic parameters	Original		Treated
	Step I	Step II	
n	1	1	1
A (s^{-1})	3.5×10^6	1×10^{11}	1.8×10^4
E (kcal mol^{-1})	19	31	15

effects. This is the reason why in the last line of Table 3 the kinetic constants are given for the same temperature. This facilitates a comparison between the decomposition rates of the two different steps.

A comparison of these data with those obtained for the thiobenzamide shows that substitution at the nitrogen atom induced major changes in the thermal, physical and chemical behaviour of the material.

The thermal curves of *N*-methylthiocinnamamide are given in Fig. 5. The significant points are: melting at 125°C and a single decomposition step at



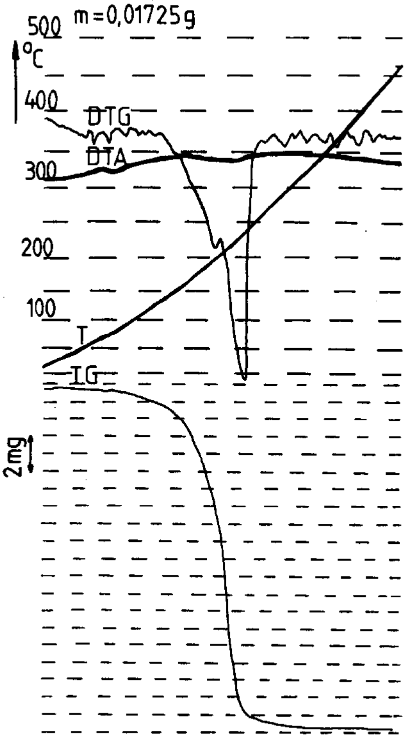


Fig. 3. Derivatogram of the original recrystallized *N*,*N*-dimethylthiobenzamide.

Fig. 4. Derivatogram of the treated *N*,*N*-dimethylthiobenzamide.

TABLE 3

Non-isothermal kinetic parameters for *N*,*N*-dimethylthiobenzamide

Kinetic parameter	Step I		Kinetic parameter	Step II	
	Original	Treated		Original	Treated
n	1	1	n	1	1
A (s^{-1})	2.2×10^{5}	6.8×10^{25}	A (s^{-1})	1.1×10^{14}	6.5×10^{18}
E (kcal mol^{-1})	15.8	58.8	E (kcal mol^{-1})	37.5	47.3
k_{468} (s^{-1}) [a]	8.6×10^{-3}	1.8×10^{-2}	k_{505} (s^{-1})	5.5×10^{-3}	2.0×10^{-2}

[a] k_T = kinetic constant at temperature T (K).

280°C. The thermal treatment does not induce any change in the chemical thermal behaviour of the substance. The non-isothermal kinetic parameters of the decomposition are: $n = 1$; $A = 1.5 \times 10^4$ s^{-1}; $E = 16.8$ kcal mol^{-1}. The value of $n = 1$ is characteristic of unimolecular liquid-phase decomposition but the relatively low value of the pre-exponential factor with respect to that predicted by the transition state theory [5] suggests some physical kinetic limitations.

The derivatograms recorded for *p*-methoxythiocinnamamide and *p*-chlo-

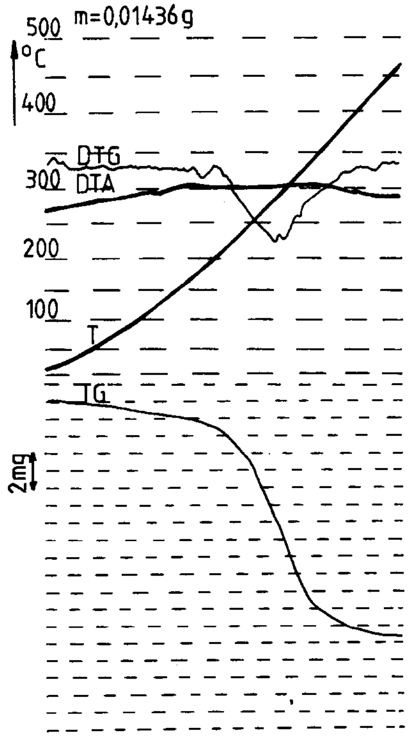


Fig. 5. Derivatogram of the original recrystallized *N*-methylthiocinnamamide.

rothiocinnamamide are similar to that of thiocinnamamide. Thus, substitution in the aromatic ring does not induce major changes in the thermal chemical behaviour.

CONCLUSIONS

(1) An investigation concerning the thermal behaviour of some substituted thioamides was performed.

(2) Substitution at the nitrogen atom induces some changes in the thermal decomposition curves.

(3) The thermal curves exhibit the existence of two species for *N*-methylthiobenzamide and *N*,*N*-dimethylthiobenzamide. The derivatographic data are confirmed by crystallinity data.

(4) The thermal decomposition curves are influenced to a lesser extent by substitution in the aromatic ring.

(5) All the decompositions lead only to gaseous products.

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