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STUDY OF THE THERMAL PROPERTIES OF 1,4-DISUBSTITUTED THIOSEMICARBAZIDES

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A study was made of the thermal degradations of 1.4-disubstituted thiosemicarbazides of general formula R^1-CH-/CO_2R^2/-NH-CS-NH-NH-R^3, which lead to the formation of cyclic 3-aminothiohydantoins. The rate of cyclization was determined by DTG and compared with the semiquantitative results of DTA which are influence by the melting of the substances examined. The R^1-substituted 3-aminothiohydantoins produced by cyclization undergo further thermal decomposition, with evolution of hydrogen sulphide as a low-molecular volatile product and formation of a polymeric residue characterized by a considerable stability.

Introduction

The aim of this work was to study the thermal properties of the series of substances whose structures and names are shown in Table 1.

Compounds Ia–VIIa are crystalline compounds, whose melting is accompanied by a chemical reaction giving rise to a volatile product. It was assumed that this was the formation of the cyclic 3-aminothiohydantoins Ib–VIIb.

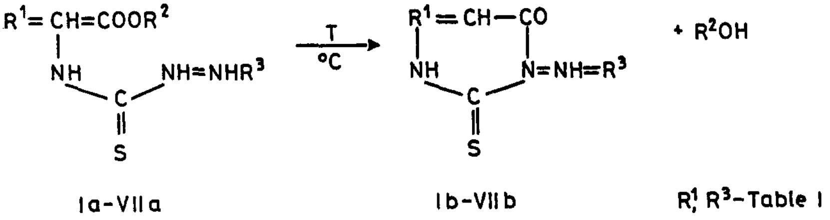

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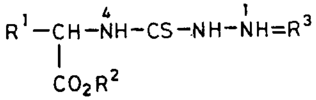
Table 1 Application of 1.4-disubstituted thiosemicarbazides



$$R^1-\underset{\substack{|\\ CO_2R^2}}{CH}-\overset{4}{N}H-CS-NH-\overset{1}{N}H=R^3$$

No.	R^1	R^2	R^3	
Ia	H	CH_3	H	4-methoxycarbonylmethyl thiosemicarbazide
IIa	H	C_2H_5	H	4-ethoxycarbonylmethyl thiosemicarbazide
IIIa	H	C_2H_5	isonicotinoyl	4-ethoxycarbonylmethyl-I- -isonicotinoylthiosemicarbazide
IVa	$HOC_6H_4CH_2$	C_2H_5	isonicotinoyl	4-[/1'-ethoxycarbonyl-2'- -/4-hydroxyphenyl/ethyl] 1-isonicotinoylthiosemicarbazide
Va	$CH_3CH/CH_3/CH_2$	C_2H_5	isonicotinoyl	4-[/1'-ethoxycarbonyl-3'- -methyl/butyl/]-1-isonicotinoylthiosemicarbazide
VIa	$C_6H_5CH_2$	C_2H_5	isonicotinoyl	4-[/1'-ethoxycarbonyl-2'- -phenyl/ethyl]-1-isonicotinoylthiosemicarbazide
VIIa	$CH/CO_2C_2H_5/CH_2CO_2$	C_2H_5	isonicotinoyl	4-[/1',1'-bis-ethoxycarbonyl]- -4'-isonicotinoylthiosemicarbazide

In addition, the substituents R^1 and r^2 and particularly R^3 were presumed to influence the stability of the material examined. The extent of this was detectable via the kinetic parameters relating to the splitting-off of the alcohol R^2OH, which was studied by means of thermogravimetry [1] and semiquantitative differential thermal analysis [2].

Experimental

Materials

The isothiocyanates used were synthesized by the thiophosgene method [3].

1-Acyl-4-R-3-thiosemicarbazides [4]

The appropriate isothiocyanate (0.01 mole) in ethanol (5 ml) was added dropwise to the acid hydrazide (0.01 mole) or to hydrazine hydrate (50% aqueous solution) dissolved in ethanol (20 ml) under heating. After refluxing for 2 h and cooling, the crystalline compounds I-VIIa were formed; they were recrystallized from ethanol (Table 1).

Thermal analysis

All measurements were made in a dynamic atmosphere of nitrogen ($3\ \mathrm{l\cdot h^{-1}}$), using a Mettler Thermoanalyzer 1 at a constant heating rate of 4 $\mathrm{deg\cdot min^{-1}}$ with Pt/Pt-Rh thermocouples; Al_2O_3 was used as a standard for DTA; the DTA sensitivity was 100 V. The activation energy (E) was calculated via the following Eq. (1):

$$\ln - \ln(1-\alpha) - 2n \ln T = -\frac{E}{RT} + n \ln \frac{nA\,1/nR}{E \cdot \beta}$$

Compound IIb was isolated after the thermal decomposition of IIa.
^{1}H-NMR: 10.06 /s, 1H, NH/, 4.96 /s, 2H, NH_2/, 4.03 /s, 2H, CH_2/.
^{13}C-NMR: 183.55 /s, C-2/; 196.42 /s, C-4/; 46.99 /t, C-5/.

^{1}H- and ^{13}C-NMR spectra were obtained on a Brucker AM 300 instrument equipped with an Aspect 3000 data system, against D_6-DMSO.

Results and discussion

Figure 1 shows the thermoanalytical curves (TG, DTG and DTA) for 4-ethoxycarbonylmethylthiosemicarbazide (IIa) and the TG curve for Ia. Both substances begin to decompose thermally during melting, the first step of active thermal decomposition corresponding to the splitting-off of a molecule of alcohol /methanol or ethanol/. The weight loss for substance Ia is to be seen from Fig. 1 and Table 2.

When R^3 = isonicotinoyl, the initial temperature required for the splitting-off of ethanol is higher, and the formation of 3-aminothiohydantoin proceeds at a lower rate (Table 2).

For Va–VIIa, the splitting-off of ethanol is promoted to approximately the same extent, but the initial temperatures for the start of this reaction differ. The maximum is achieved (in accordance with assumptions) for the substance with R^1 = isobutyl.

The lowest rate of splitting-off of ethanol was measured for the substance IVa, containing R^1 = 4-hydroxybenzyl.

When the determined apparent activation energies are compared with the defined enthalpies [5] of the endothermic changes, certain differences are observed. These arise from the fact that the endothermic effects of melting and alcohol release and also the cyclization effects overlap on the DTA thermograms, while the thermogravimetric results in this temperature range seem to be unambiguous.

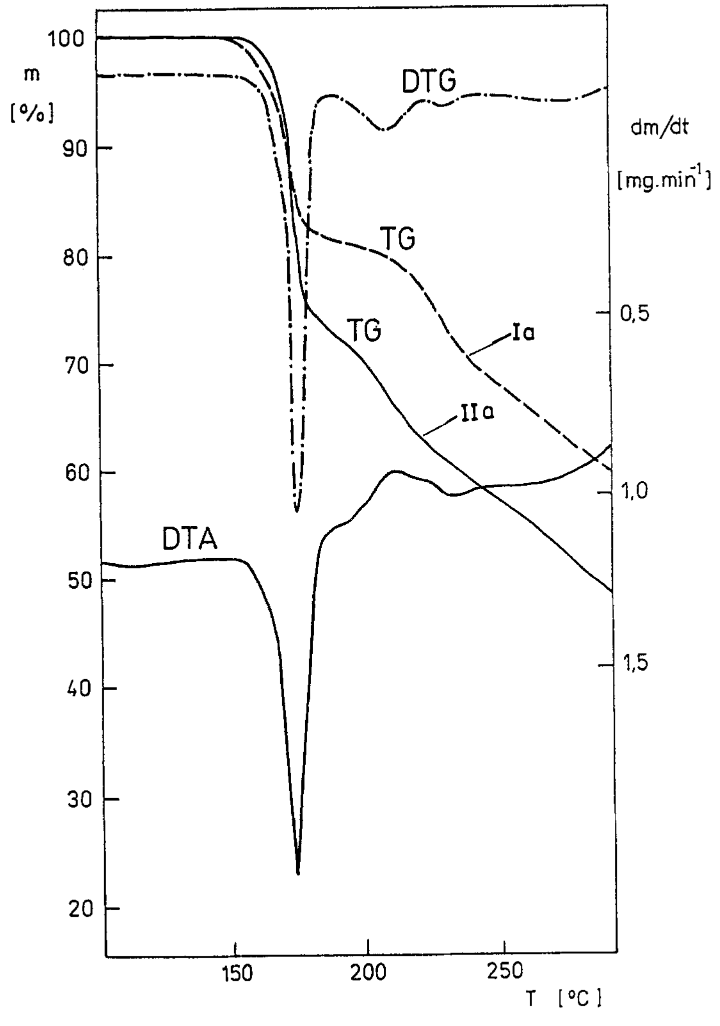


Fig. 1 TG, DTG, DTA curves of the substance IIa and TG curves of the substance Ia

The thermoanalytical curves illustrated in Fig. 1 indicate that there exists at least one additional, clearly separated step in the active decomposition. The decompositions of Ia and Ib proceed at approximately the same maximum rate and at 207°C, which confirms the production of the identical 3-

Table 2 The results of thermal analysis of 1.4-disubstituted thiosemicarbazides

Subst. No.	M.p./	DTA		TG			E /	A /
	°C	T (endo)	ΔH / kJ · kg^{-1} [2]	T_{poc}	T_{max}	W_{max}	kJ · mol^{-1} [1]	s^{-1}
Ia	169–170	152	424	135	154	1.05	206	$1.7 \cdot 10^{22}$
IIa	172–174	178	525	164	180	2.00	347	$1.7 \cdot 10^{37}$
IIIa	196–198	198	360	185	199	1.37	312	$2.2 \cdot 10^{31}$
IVa	185–186	185	220	172	185	0.85	248	$9.7 \cdot 10^{24}$
Va	204–206	214	235	194	215	1.20	243	$4.7 \cdot 10^{24}$
VIa	190–192	201	466	190	203	1.20	253	$1.0 \cdot 10^{24}$
VIIa	172–174	178	328	166	180	1.20	303	$1.0 \cdot 10^{30}$

aminothiohydantoins on thermolysis of Ia and IIa after the splitting-off of alcohol. Moreover, the thermal decompositions of the 3-amino- thiohydantoins Ib–VIIb lead to the formation of H_2S as a low-molecular volatile product (from GC). However, in the condensed phase subsequent exothermic reactions take place (Fig. 1).

Substances IIa–VIIa differ one from another in the course of the second step of active degradation. The temperature of the maximum rate of this reaction rises up to 300°C or more, and the rate increases from 0.15 up to 0.9 mg/min. At 350°C, Ia–VIIa all leave a polymeric residue (which is characterized by a relatively high thermal stability (Table 3).

The least thermally stable appears to be the polymeric product formed from the aminothiohydantoins of Vb (27.2%).

Table 3 The results of thermal analysis for the second step of thermal decomposition

Substance No.	T_{init} / °C	T_{max} / °C	V_{max} / mg·min^{-1}	$R_{35^{\cdot}}$ / %
Ib	187	211	0.30	48.9
IIb	189	211	0.25	45.7
IIIb	210	278	0.40	33.3
IVb	246	300	1.00	50.0
Vb	246	300	0.90	27.2
VIb	248	302	0.81	39.7
VII.b	207	259	0.62	40.1

The aminothiohydantoin of IVb, which undergoes the most rapid decomposition, provides as much as 50% of the resistant residue at 350°C. This product has the characteristics of nitrogen-containing polymeric substances.

References

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Zusammenfassung — Es wurde der thermische Abbau von 1,4-disubstituierten Thiosemikarbaziden der allgemeinen Formel R^1-CH-(CO_2R^2)-NH-CS-NH-NH-R^3 mit Bildung von cyclischen 3-Aminothiohydantoinen untersucht. Mittels DTG wurde die Geschwindigkeit der Cyclisierung bestimmt und mit den semiquantitativen DTA-Ergebnissen, die durch das Schmelzen der untersuchten Substanzen beeinflußt werden, untersucht. Die bei der Cyclisierung entstehenden R^1-substituierten 3-Aminothiohydantoine unterliegen einer weiteren thermischen Zersetzung, wobei als niedermolekulares flüchtiges Produkt Schwefelwasserstoff gebildet wird und ein beträchtlich stabiler polymerer Rückstand entsteht.