

THERMAL PROPERTIES OF 5-(SUBST)-AMINO-1,2,3,4-THIATRIAZOLES

L. FLOCH, A. MARTVOŇ and M. KOŠIK

Faculty of Chemistry and Technology of the Slovak Technical University,
Jánska 1, 88037 Bratislava, Czechoslovakia

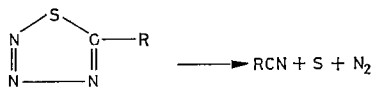
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The thermal properties of 5-(subst)-amino-1,2,3,4-thiatriazoles were studied using TG and DTA. 5-amino-1,2,3,4-thiatriazole was actively decomposed at the melting temperature. The active thermal decomposition proceeds at a very fast rate, being accompanied by exothermic reactions of recombination. In comparison with this, the different-5-(subst)-amino-1,2,3,4-thiatriazoles are decomposed at slower rates in several degradative steps. The effects of some substituents on the total course of thermal degradation are discussed.

5-(substituted)-amino-1,2,3,4-thiatriazoles are not stable to heating. Their thermal instability is mostly dependent on the character of the substituent [1]. Moreover, 5-alkoxy-[2] and 5-alkyl-1,2,3,4-thiatriazoles [3] are unstable even at room temperature. 5-aryl derivatives appear to be more stable [4], their higher thermal stability being observed in the presence of electron-acceptor groups [5].

5-amino-1,2,3,4-thiatriazole decomposes on heating and the formation of dicyanamide can be detected [6, 7]. The thermal decompositions of other 5-(subst)-amino-1,2,3,4-thiatriazoles have not been studied until now.

According to several references [6, 7], the thermal decompositions of 5-(subst)-1,2,3,4-thiatriazoles proceed in the following way:



In this paper, the results of thermal analysis (DTA, TG, DTG) of 5-(subst)-amino-1,2,3,4-thiatriazoles will be presented. Special attention will be given to 5-(1-carboxyalkyl)-amino-1,2,3,4-thiatriazoles, because the course of thermal decomposition of this type of compound is interesting from a practical point of view.

Experimental

Synthesis

The list of compounds (I – VIII) investigated is given in Table 1. 5-amino-1,2,3,4-thiatriazole (I) was prepared by the action of nitric acid on the thiosemicarbazide [8] and then purified by multiple crystallization from an ethanol – water mixture.

Table 1
 Thermal properties of 5-/substituted/amino-1,2,3,4-thiazotriazoles

	R	Melting		Active degradation						Residue at 500, %		
		Kofler, °C	DTA, °C	exothermic decomposition		endothemic decomposition		endothemic decomposition				
				t_{max} , °C	Δm , %	t_{max} , °C	Δm , %	t_{max} , °C	Δm , %			
I	H-	125-6	114	126	1.5	86	-	-	-	-	-	0
II	C ₆ H ₅	142.5	145	149	1.2	69	249	0.07	11	392	0.1	3
III	C ₆ H ₅ CH ₂	68-9	74	87	0.24	17	248	0.21	-	288	0.18	75
IV	CH ₂ CO ₂ C ₂ H ₅	69-69.5	74	92	0.32	20	129	0.10	10	214	0.13	21
V	CH ₃ CH(CO ₂ C ₂ H ₅)	84.5-86	91	99	0.38	18	186	0.28	26	230	0.10	13
VI	C ₂ H ₅ CH(CO ₂ C ₂ H ₅)	64.5-65.5	70	100	0.20	18	194	0.23	28	229	0.12	14
VII	<i>n</i> -C ₄ H ₉ CH(CO ₂ C ₂ H ₅)	37-8	44	93	0.15	16	170	0.08	18	246	0.14	21
VIII	C ₆ H ₅ CH ₂ CH(CO ₂ C ₂ H ₅)	97.5-98	104	106	0.44	10	192	0.12	14	253	0.08	24
										311	0.11	

Compounds II–VIII were prepared by the reaction of the relevant isocyanate with the azoimide or trimethylsilylazide [9]. They were crystallized from an ethanol – petrolether – tetrahydrofuran mixture and then dried under reduced pressure before measurements were made. The purities of the compounds obtained were controlled by t.l.c., elemental analysis and IR spectra [9].

Thermal analysis

All measurements were made in a dynamic atmosphere of nitrogen – (7 l h^{-1}) using a Mettler Thermoanalyser 2 at the constant heating rate of 6° min^{-1} . Pt/Pt Rh thermocouples were used, with Al_2O_3 as a standard for DTA.

Spectral analysis

IR spectra were recorded with the Zeiss-Jena UR-20 equipment and spectral chloroform as solvent. The accuracy of frequency measurements was $\pm 1\text{ cm}^{-1}$.

Discussion

The thermal decomposition of 5-(subst)-amino-1,2,3,4-thiatriazoles was studied by methods of thermal analysis. The thermal behaviour of compounds I–VIII is shown in Table 1. The DTA, TG and DTG curves for 5-amino-1,2,3,4-thiatri-

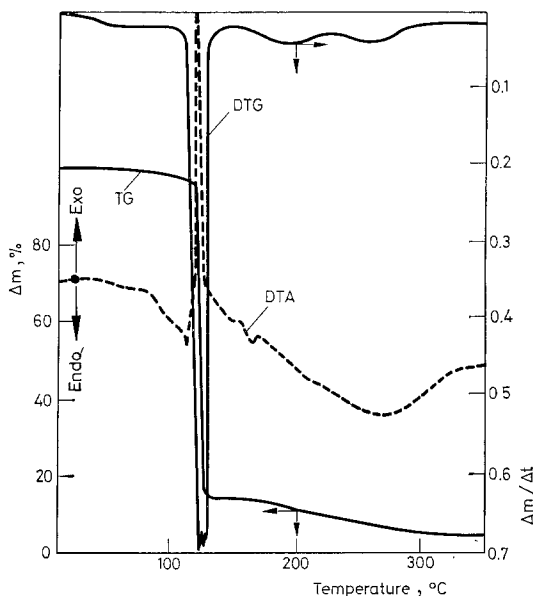


Fig. 1. DTA, TG and DTG curves of 5-amino-1,2,3,4-thiatriazole

azole are illustrated in Fig. 1, which indicates that the thermal decomposition of this type of compound occurs approximately at the melting point and is very fast (DTG). The decomposition is accompanied by 80% weight loss and exothermic reactions of fragment recombination (DTA). The active degradation of the residue, which has a very slow and endothermic character, proceeds at temperatures above 200° and is completed at 500°.

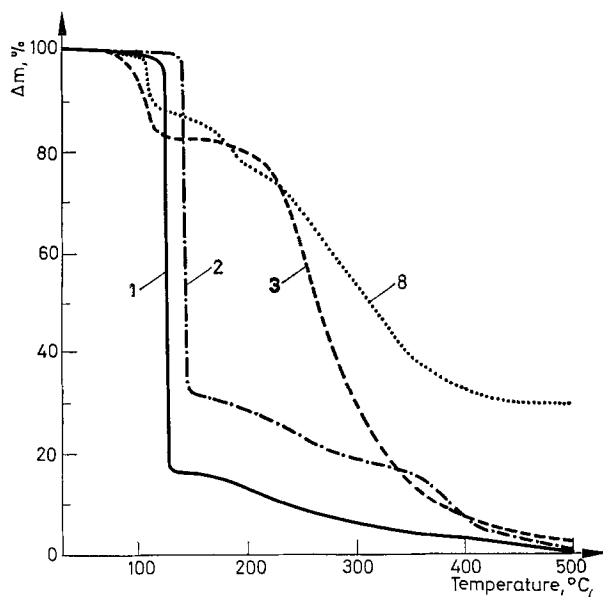


Fig. 2. TG curves of compounds I, II, III and VIII denoted as Table 1

From a comparison of the active thermal degradation of compounds I, II and III (Fig. 2) it can be concluded that substitution of protons in 5-amino-1,2,3,4-thiazotriazole (I) with phenyl (II) or benzyl (III) increases the thermal stability. The first active degradation step for compounds II and III proceeds at a lower rate and with a smaller weight loss than in the case of compound I. A further increase in thermal stability was attained by introducing carboxy substituents in position 5. The residue produced after the first degradation stage is decomposed in two different stages and the total weight loss at 500° is smaller for compounds IV–VIII than for I–III. The effects of various substituents on the overall course of thermal degradation of 5-(subst)-amino-1,2,3,4-thiazotriazoles is given in Table 1.

The residue produced after the first degradation stage was also studied using IR spectra. From the main results presented in Table 2 it can be concluded that during the first stage of decomposition the relevant substituted cyanimides are formed. The isolation of pure products was not successful because the compounds primarily formed were very reactive, and the formation of high molecular weight condensates was observed.

References

1. K. A. JENSEN and C. PEDERSEN, *Advances in Heterocycl. Chem.*, Vol. 3, Academic Press, New York, 1964, p. 263.
2. K. A. JENSEN, A. HOLM and B. HORKILSEN, *Acta Chem. Scand*, 18 (1964) 825.
3. E. LIEBER, C. N. R. RAO and R. C. ORLOWSKI, *Can. J. Chem.*, 41 (1963) 926.
4. W. KIRMSE, *Chem. Ber.*, (1960) 2353.
5. P. A. S. SMITH and D. H. KENNY, *J. Org. Chem.*, 26 (1961) 5221.
6. M. FREUND and A. SCHANDER, *Chem. Ber.*, 29 (1896) 1500.
7. E. LICBER and C. N. PILLAI, *J. Org. Chem.*, 22 (1957) 1054.
8. M. FREUND and H. P. SCHWARZ, *Chem. Ber.*, 29 (1896) 2491.
9. L. FLOCH, A. MARTVOŇ and M. UHER, *Coll. Czech. Chem. Com.* (in press).

RÉSUMÉ — On a étudié par TG et ATD les propriétés thermiques des 5-(subst)-amino-1,2,3,4-thiatriazoles. Le 5-amino-1,2,3,4-thiatriazole se décompose activement à la température de fusion. La décomposition thermique active s'effectue avec une très grande vitesse et s'accompagne de réactions exothermiques de recombinaison. Par contre, les divers 5-(subst)-amino-1,2,3,4-thiatriazoles se décomposent avec une vitesse plus faible et en plusieurs étapes. On discute l'effet de quelques substituants sur le processus complet de la dégradation thermique.

ZUSAMMENFASSUNG — Die thermischen Eigenschaften von 5-(subst)-Amino-1,2,3,4-Thiatriazolen wurden mittels der Methoden TG und DTA untersucht. Das 5-Amino-1,2,3,4-Thiatriazol wurde bei der Schmelztemperatur aktiv zersetzt. Die aktive thermische Zersetzung verläuft mit einer sehr großen Geschwindigkeit und wird von den exothermen Reaktionen der Rekombination begleitet. Im Vergleich hierzu werden die verschiedenen 5-(subst)-Amino-1,2,3,4-Thiatriazole mit einer geringeren Geschwindigkeit, in mehreren Zersetzungsstufen abgebaut. Die Wirkung einiger Substituenten auf den Gesamtverlauf der thermischen Zersetzung wird erörtert.

Резюме — Были изучены, используя методы ТГ и ДТА, термические свойства 5-(замещенных)-амино-1,2,3,4-тиатриазолов. 5-амино-1,2,3,4-тиатриазол активно разлагался уже при температуре плавления. Это активное термическое разложение протекает с очень высокой скоростью, сопровождаясь экзотермическими рекомбинационными реакциями. По сравнению с этим соединением, другие 5-(замещенные)-амино-1,2,3,4-тиатриазолы разлагаются более медленно в несколько ступеней. Обсуждено влияние некоторых заместителей на общий ход термического разрушения.