

# Study of thermal decomposition of tetramethylthiuram disulfide

E. ŠTAUDNER, J. BENISKA, and G. KYSELÁ

*Department of Chemical Technology of Plastics and Fibers,  
Slovak Technical University, 880 37 Bratislava*

Received 25 September 1975

*Dedicated to Professor RNDr J. Gašperík on his 70th birthday*

Thermal decomposition of tetramethylthiuram disulfide (TMTD) in solid form was studied by means of thermal analysis and mass spectroscopy. It was found that the decomposition of TMTD in solid phase is complicated and a series of primary and secondary decomposition products is formed as a consequence of the induced chain process. A scheme describing this thermal decomposition of TMTD was proposed.

В работе исследовалось термическое разложение тетраметилтиурам-дисульфид (ТМТД) в твердой фазе методом термического анализа и массовой спектроскопии. Было установлено, что разложение ТМТД в твердой фазе сложное, возникает целый ряд первичных и вторичных продуктов разложения как следствие индуцированного цепного процесса. Это позволило создать схему описывающую термическое разложение ТМТД.

In the study of the influence of tetramethylthiuram disulfide on the polymerization of reactive monomers it was found [1—4] that TMTD is decomposed in the presence of monomers already at relatively low temperatures (60—80°C).

TMTD acts as an inhibitor at the polymerization of acrylonitrile (AN) and vinyl acetate (VAc), initiated by benzoyl peroxide, which was explained by the predominant participation of TMTD radicals in termination reactions [5, 6].

On the other hand, some authors [7] ruled out the possibility of the formation of radicals during the thermal decomposition of TMTD up to 140—150°C and proposed an ionic (polar) mechanism for the vulcanization process.

The aim of this work was to analyze the mechanism of the thermal decomposition of TMTD in solid phase at temperatures comparable with those used in the polymerization.

## Experimental

Tetramethylthiuram disulfide — technical grade (produced by CHZJD, n.e., Bratislava) was used. It was purified by a fourfold precipitation with methanol from a  $\text{CHCl}_3$  solution and by a twofold recrystallization from  $\text{CHCl}_3$ . It was dried *in vacuo* and stored in dark at room temperature.

The thermal analysis was carried out using a Mettler II apparatus. Measuring conditions: initial weight of the sample 7.5 mg, temperature range 0–500°C, heating rate 6°C/min, sensitivity TG 10/1 mg and 10× exp., DGT 1 mg/min, DTA 50 μV, gas flow: nitrogen 7 l/hr, air 7 l/hr.

The mass spectroscopy was carried out using Atlas CH-4 and Varian MS 902 S devices. The pyrolysis took place directly in the devices *in vacuo* at 70, 84, and 90°C. Ionization potential: 70 eV. The initial weight of the samples was 1–2 mg.

### Experimental results and discussion

The thermal analysis was carried out under the same conditions in the air and in the nitrogen atmosphere. The thermograms are shown in Figs. 1 and 2.

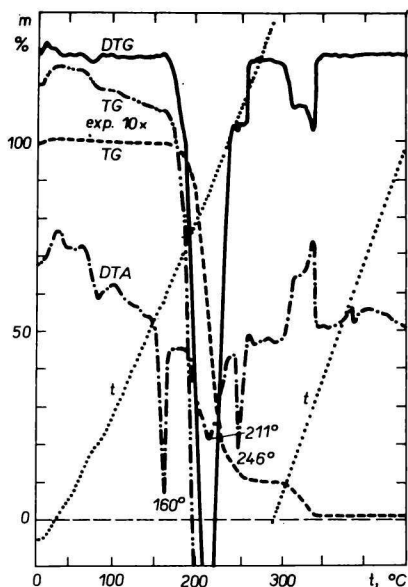


Fig. 1. Thermogram of TMTD in air.

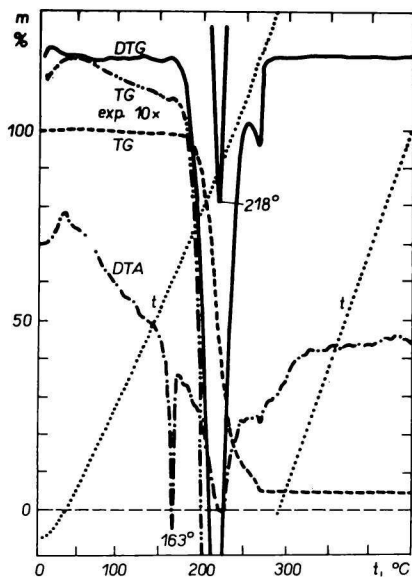


Fig. 2. Thermogram of TMTD in nitrogen atmosphere.

The thermal analysis of TMTD in air as well as in nitrogen atmosphere showed (Figs. 1 and 2, curves TG exp.) that its thermal decomposition under the formation of volatile products (probably  $\text{CS}_2$ ,  $(\text{CH}_3)_2\text{N}$  and others) starts already at relatively low temperatures, 50–55°C, below the melting point (melting point in air 159–161°C, in nitrogen 163°C). Up to the melting point of TMTD 1.2% of volatile products is released. In the temperature range 60–100°C a small endothermic peak with a maximum at 85°C was observed. The weight loss can be influenced to some extent by evaporation of residual solvents ( $\text{CHCl}_3$ ).

According to the TG curve (Fig. 1) the decomposition in the presence of air is accomplished in three steps. The first endothermic decomposition step appears in the temperature range 155—235°C. The weight loss in this step was 82%. The second endothermic step appears in the temperature range 235—255°C, with weight loss 7%. The second melting point was observed at 246°C and it was ascribed to the oxidation product formed in the first degradation step. The third step in the temperature range 300—340°C is exothermic. The weight loss in this step was 9.3% and there remained a small amount of residue (less than 1%).

The thermal decomposition of TMTD in an inert atmosphere occurs in two steps as seen from the TG curves (Fig. 2). The first, endothermic step is much more expressive than in the presence of air and occurs in the temperature range 155—245°C. The weight loss in this step was 85%. The second step, endothermic also in the temperature range 245—260°C was accompanied by a weight loss of 9.3%. The carbonized residue amounted to 4.5%.

The formation of volatile products observed during the heating of TMTD at 50—100°C indicates that the thermal decomposition takes place even at relatively low temperatures.

The intense decomposition of TMTD begins close to the melting point and the great weight loss may be related to the induced chain mechanism of decomposition.

In the study of the TMTD decomposition on mass spectrometers it was found that the decomposition of TMTD in solid phase is a very complicated process in which a series of primary and secondary decomposition products is formed. The survey of the most important bands and their relative intensities are given in Table 1.

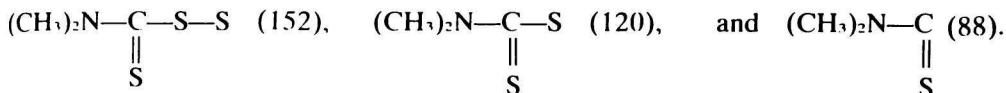
The most intensive bands belong to the cations with  $m/e$  values: 42, 44, 72, 73, 76, 77, 88, 120, and 240. The relative intensity of the bands is changing with the temperature of pyrolysis.

The presence of the bands 120, 152, 88, and 64 indicated that during the pyrolysis TMTD is decomposed both symmetrically (on S—S bond) and asymmetrically (on C—S bond).

The cations found in the mass spectra are partly the primary products of pyrolysis and of the ionization effect and partly the secondary products of a spontaneous conversion or of a decomposition of the primary products of pyrolysis and ionization.

From the analysis of the mass spectra it is evident that during the thermal decomposition of TMTD in the absence of acceptors of radicals or ions a number of parallel and successive reactions with chain mechanism takes place. The thermal decomposition of TMTD in solid phase interpreted on the basis of mass spectroscopy results is shown in Scheme 1.

The mass spectroscopy analysis of products of the TMTD pyrolysis showed the primary products of the thermal decomposition to be fragments of the type



The secondary products of the decomposition of primary products of pyrolysis and ionization are fragments of the type

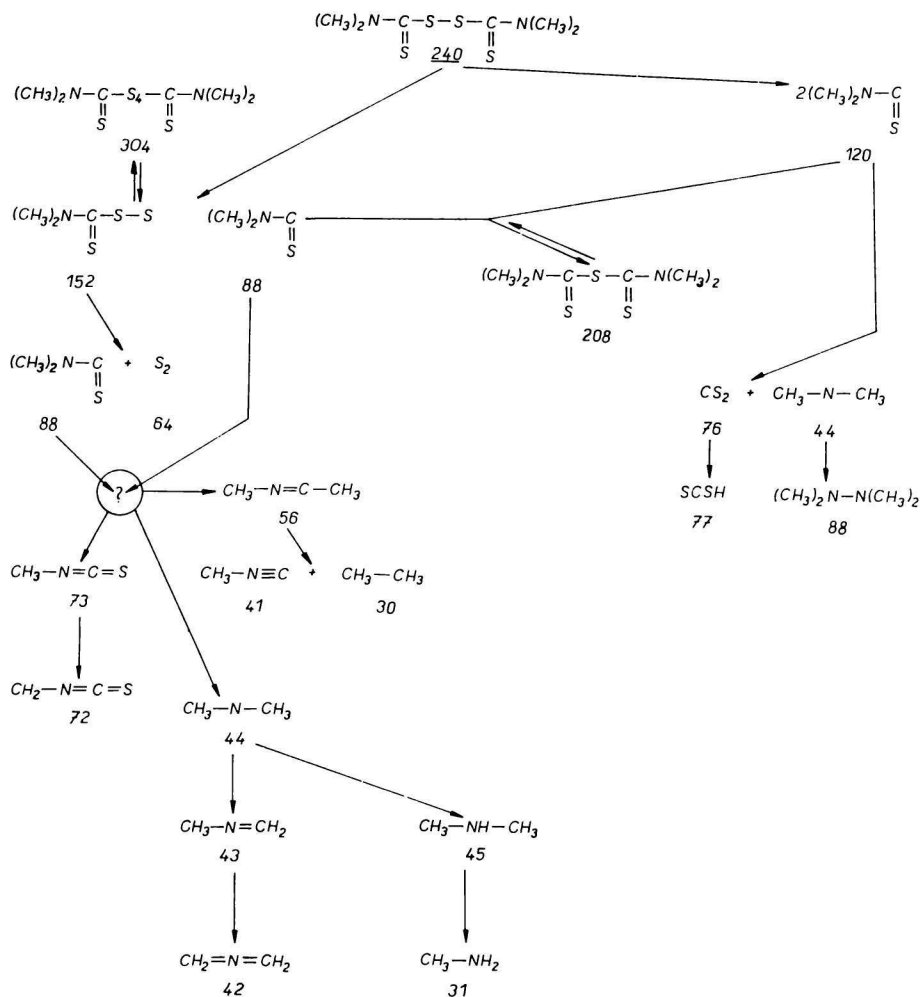


with bands of a high intensity in the mass spectra.

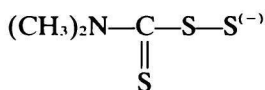
Table 1

Main bands in mass spectra of TMTD

<i>m/e</i>	Cation type	% RI		
		70°C	84°C	90°C
42	$\text{CH}_2=\text{N}=\text{CH}_2$	23.8	34.6	98.0
43	$\text{CH}_2=\text{N}-\text{CH}_3$	6.3	9.5	37.0
44	$\text{CH}_3-\text{N}-\text{CH}_3$	25.0	36.3	96.0
45	$\text{CH}_3-\text{NH}-\text{CH}_3$	8.1	11.9	49.0
47	?	6.0	8.8	29.0
56	$\text{CH}_3-\text{N}=\text{C}-\text{CH}_3$	7.3	10.4	36.0
64	$\text{S}_2$	3.3	8.9	30.0
72	$\text{CH}_2-\text{N}=\text{C}=\text{S}$	6.9	11.5	63.0
73	$\text{CH}_3-\text{N}=\text{C}=\text{S}$	15.4	22.1	98.0
76	$\text{CS}_2$	24.2	33.7	28.0
77	SCSH	8.5	12.9	93.0
88	$(\text{CH}_3)_2\text{N}-\text{C}=\text{S}; (\text{CH}_3)_2\text{N}-\text{N}(\text{CH}_3)_2$	100	100	100
89	$(\text{CH}_3)_2\text{N}-\text{C}-\text{H}; (\text{CH}_3)_2\text{NH}-\text{N}(\text{CH}_3)_2$	9.1	12.1	23.5
120	$(\text{CH}_3)_2\text{N}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{S}$	6.0	15.4	92.0
121	$(\text{CH}_3)_2\text{N}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{SH}$	17.3	23.8	5
152	$(\text{CH}_3)_2\text{N}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{S}-\text{S}$	0.5	1.3	7.0
208	$(\text{CH}_3)_2\text{N}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{S}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{N}(\text{CH}_3)_2$	11.0	10.4	5
240	$(\text{CH}_3)_2\text{N}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{S}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{N}(\text{CH}_3)_2$	6.0	14.0	88.0
303	$(\text{CH}_3)_2\text{N}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{S}_4-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{N}-\text{CH}_3$	0.5	7.5	—
305	$(\text{CH}_3)_2\text{N}-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{S}_4-\underset{\text{S}}{\underset{\parallel}{\text{C}}}-\text{NH}(\text{CH}_3)_2$	0.4	4.7	—



The high intensity of the band 88 and the low intensity of the band 152 can be related to the direct heterolytic decay of the C—S bond in TMTD resulting from its natural polarization. The low intensity of the band 152 is then caused by the formation of an anion of the type



which is not recorded on the mass spectrope.

At temperatures 70 and 84°C also the bands corresponding to the ions of

tetramethylthiuram monosulfide 208 and of tetramethylthiuram tetrasulfide 303 and 305 were determined. These bands were not observed at 90°C.

The results of the study of thermal decomposition of TMTD in solid phase showed that in the absence of acceptors of radicals the decomposition is a very complicated process involving a series of primary and secondary products. The results indicate the likely induced chain-like course of the TMTD decomposition.

*Acknowledgements.* The authors wish to express their thanks to Dr V. Reiser for the thermoanalytical measurements, to Dr E. Špírk for measuring the mass spectra on the Atlas Ch-4 device, and to J. Ivanová for the technical cooperation.

### References

1. Ferington, T. E. and Tobolsky, A. V. *J. Amer. Chem. Soc.* **77**, 4510 (1955).
2. Štaudner, E., Beniska, J., and Znamenáková, G., *Chem. Zvesti* **20**, 18 (1966).  
Beniska, J. and Štaudner, E., *J. Polym. Sci., C*, **16**, 1301 (1967).
4. Štaudner, E. and Beniska, J., *Eur. Polym. J., Supplement* **1969**, 537.  
Beniska, J., *Vysokomol. Soedin.* **13**, 1790 (1971).
6. Beniska, J. and Štaudner, E., *J. Polym. Sci.* **42**, 429 (1973).
7. Bateman, L., *The Chemistry and Physics of Rubberlike Substances*, p. 784. Interscience, New York, 1963.

Translated by P. Rosner