Thermochimica Acta, 105 (1986) 239–245
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ON THE THERMAL STABILITY OF SOME 3,5-DISUBSTITUTED 1,2,4-THIADIAZOLS AND 3,5-DISUBSTITUTED-1,2,4-DITHIAZOLIN IODONIUM SALTS

FELICIA CORNEA and LUCIA IVAN

Chair of Organic and Technologic Chemistry, Faculty of Chemical Technology,
Polytechnical Institute of Bucharest, Splaiul Independentei 202, Bucharest (Romania)

IULIANA PESCARU and E. SEGAL

Chair of Physical Chemistry and Electrochemical Technology, Faculty of Chemical Engineering,
Bulevardul Republicii 13, Bucharest (Romania)

(Received 10 February 1986)

ABSTRACT

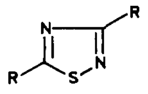
The results of a derivatographic study and a non-isothermal kinetic analysis of the decomposition of some 3,5-disubstituted-1,2,4-thiadiazols and 3,5-disubstituted-1,2,4-dithiazolin iodonium salts are presented.

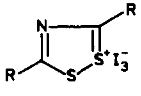
INTRODUCTION

Following our early research on the thermal stability of organic solids [1,2] this paper deals with the thermal decomposition of some 3,5-disubstituted-1,2,4-thiadiazols and 3,5-disubstituted-1,2,4 dithiazolin iodonium salts.

EXPERIMENTAL

The substances illustrated, synthesized and analysed according to methods described elsewhere were used [3]. Substances III, IV, VI, VII, are new compounds.





(I) R = C_6H_5
(II) R = p-C_6H_4Cl
(III) R = C_6H_5—CH=CH
(IV) R = p-C_2H_5O—C_6H_4—CH=CH

(V) R = C_6H_5
(VI) R = C_6H_5—CH=CH
(VII) R = p-C_2H_5O—C_6H_4—CH=CH

0040-6031/86/$03.50

TABLE 1

Mean crystallite sizes (*l*)

Compound	*l* (Å)
I	202
II	270
III	amorphous
IV	299
V	amorphous
VI	amorphous
VII	278

The heating curves were recorded with a Q 1500 MOM Budapest derivatograph type Paulik-Paulik Erdey at various heating rates between 1.25 and 10 K min^{-1}. To record the X-ray diffractograms a Philips P.W. 1400 X-ray diffractometer was used. The mean crystallite sizes were estimated by Scherrer's formula [4] for the most intense diffraction line.

RESULTS AND DISCUSSION

The mean crystallite sizes for the compounds investigated are given in Table 1.

The derivatograms corresponding to substances I–VII are given in Figs. 1–7.

As seen from the thermal curves the decomposition of compounds I–IV occurs in the molten state whereas the decomposition of compounds V–VII occurs in the solid state. Compounds I and II decompose in one step only, compounds III, IV, VI and VII decompose in two steps and compound V

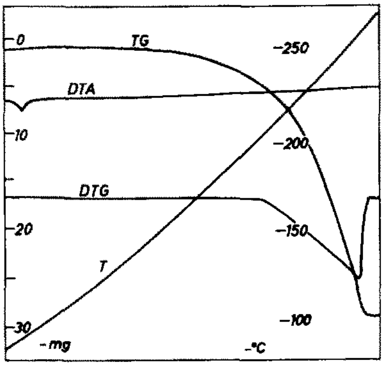


Fig. 1. Heating curves of compound I ($\beta = 2.5$ K min^{-1}).

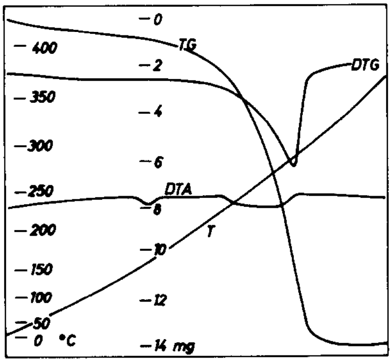


Fig. 2. Heating curves of compound II ($\beta = 5$ K min^{-1}).

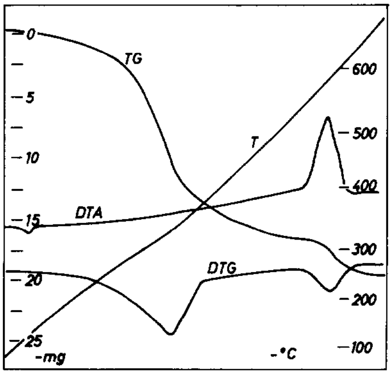


Fig. 3. Heating curves of compound III ($\beta = 10$ K min^{-1}).

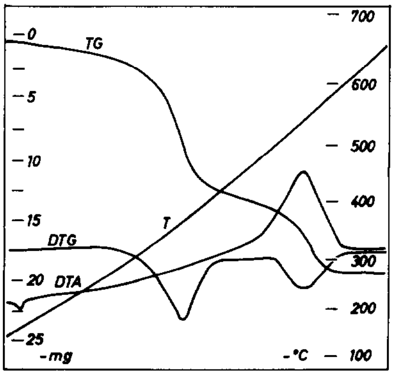


Fig. 4. Heating curves of compound IV ($\beta = 10$ K min^{-1}).

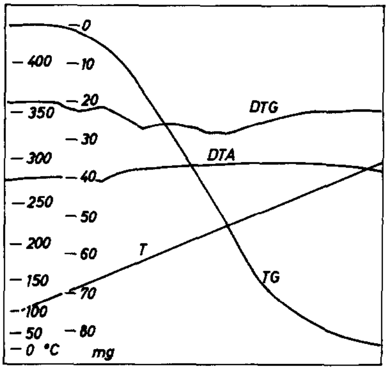


Fig. 5. Heating curves of compound V ($\beta = 1.25$ K min^{-1}).

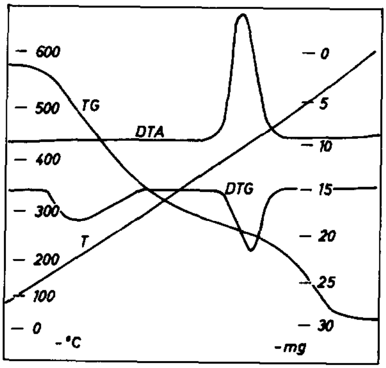


Fig. 6. Heating curves of compound VI ($\beta = 10$ K min^{-1}).

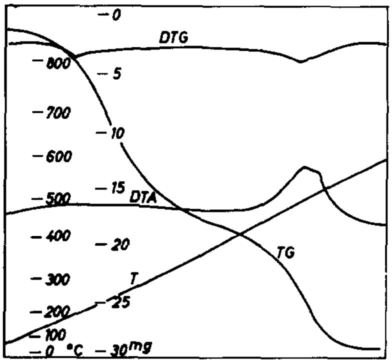
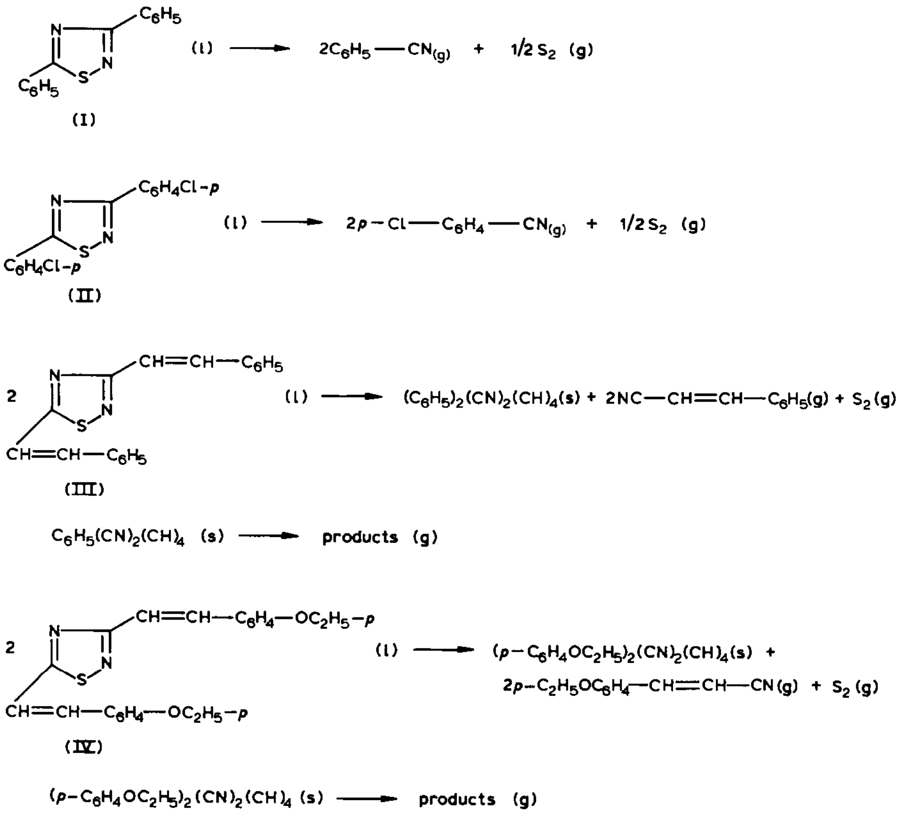


Fig. 7. Heating curves of compound VII ($\beta = 5$ K min^{-1}).

decomposes in four overlapping steps (making kinetic analyses impossible). According to the derivatographic data decomposition reactions undergone by substances I–IV are as follows



For the decomposition of substances V–VII we were not able to identify the reaction intermediates and thus the reaction stages.

The thermal curves were used to evaluate the non-isothermal kinetic parameters. To use the experimental data we applied the Coats–Redfern method [5]. The data were automatically processed by a TI 66 programmable calculator. The methods of Freeman–Carroll [6] and Ozawa [7] were also used. The values of the non-isothermal kinetic parameters (reaction order n, activation energy E and preexponential factor A) for the decomposition of compounds I–IV and VI–VII are given in Tables 2 and 3 respectively. As may be seen from Table 1 the reaction order for the first decomposition step of compounds I–IV equals zero. This could be due to diffusion tendency [8] or to vaporization of the molten substances before decomposition [9]. The value $n = 0.66$ for the decomposition of truxilic nitryls corresponds to a contracting sphere model [10].

TABLE 2

Values of the non-isothermal kinetic parameters for the decomposition of compounds I–IV

Compound	Number of step	Method						
		Coats–Redfern			Freeman–Carroll			Ozawa
		n	*E* (kcal mol^{-1})	*A* (s^{-1})	*n*	*E* (kcal mol^{-1})	*A* (s^{-1})	*E* (kcal mol^{-1})
I	1	0	14.9	1.6×10^{3}	0.1	15.5	2.6×10^{4}	12.8
II	1	0	5.0	1.7×10^{-1}	0.1	5.5	2.0×10	
III	1	0	5.0	2.3×10^{-2}	0.2	5.0	9.1×10^{-1}	
	2	0.66	44	2.8×10^{10}				
IV	1	0	14.7	2.6×10^{4}	0.1	13.0	5.3×10^{3}	13.2
	2	0.66	51.3	2.7×10^{4}	0.1	49.9	1.4×10^{13}	49.9

TABLE 3

Values of the non-isothermal kinetic parameters for the decomposition of compounds VI–VII

Compound	Number of step	Method					
		Coats–Redfern			Freeman–Carroll		
		n	*E* (kcal mol^{-1})	*A* (s^{-1})	*n*	*E* (kcal (mol^{-1})	*A* (s^{-1})
VI	1	1	4.8	3.2×10	1	4.2	1.5
	2	1	42.0	5.1×10^{13}	1	42.3	8.0×10^{13}
VII	1	1	8.3	2.0×10^{2}	0.9	8.0	6.6×10
	2	1	39.5	2.8×10^{11}	0.9	38.1	1.3×10^{10}

The value $n = 1$ obtained for the first step of the decomposition of the iodonium salts VI and VII is apparent and corresponds probably to some particular kind of nucleation of growth of the nuclei [11]. The value $n = 1$ for the second decomposition step of the iodonium salts which occurs in the liquid state seems to describe a true molecular reaction. This statement is supported by the values for the activation energy and preexponential factors typical of such reactions [12].

CONCLUSIONS

(1) A derivatographic study of some solid disubstituted thiadiazols and dithiazolin iodonium salts was carried out.

(2) The non-isothermal kinetic parameters of the decomposition reactions which occur in solid or liquid state were determined.

REFERENCES

1 F. Cornea, L. Ivan, C. Pintică and E. Segal, Thermochim. Acta, 86 (1985) 25.
2 F. Cornea, L. Ivan, C. Pintică and E. Segal, Thermochim. Acta, 87 (1985) 335.
3 (a) J.L.H. Hortmann, Justus Liebigs Ann. Chem., 650 (1977) 1005.
(b) F. Cornea, E. Segal, A. Lablache-Combier, C. Cercasov, L. Ivan and A. Ciobanu, 4th Conf. of Chemistry and Chemical Engineering, Bucharest, 1985, p. 36.
4 A. Guinier, Theorie et Technique de la Radiocristallographie, Dunod, Paris, 1964, p. 462.
5 A.W. Coats and J.P. Redfern, Nature (London), 207 (1964) 68.
6 E. Freeman and B. Carroll, J. Phys. Chem., 62 (1958) 394.
7 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
8 (a) E.I. Segal, Kinetic and Mechanismus der termischen Zersetzungsreaktionen von Komplexverbindungen, in V.V. Boldyrev and K. Meyer (Eds.), Festorperchemie, VEB Deutscher Verlag für Gründstoffindustrie, Leipzig, 1983, p. 404.
(b) I.G. Murgulescu and E. Segal, Predexponetzialnie koeffitzienti reactzii razlojenia necotorîh tverdikh heorganitcheskikh vachestv, in Gheterogenie khimitcheskie reaktzii i reaktzionnaia sposobnosti, Nauka i Technika, Minsk, 1975, p. 36 (in Russian).
9 (a) I.G. Murgulescu and E. Segal, Rev. Roum. Chim., 10 (1965) 307.
(b) E. Segal, Thesis, University of Bucharest, 1963.
10 I.G. Murgulescu, T. Oncescu and E. Segal, Introduction to Physical Chemistry, Vol. II.2 (in Romanian), Publishing House of the Academy of the Socialist Republic of Romania, Bucharest, 1981, p. 702.
11 Šesták, Thermophysical Properties of Solids, Academia, Prague, 1984, pp. 190–191.
12 H. Eyring, S.H. Lin and S.M. Lin, Basic Chemical Kinetics, Nauka i Tekhnica, Minsk, 1975, p. 36 (in Russian); Mir, Moscow, 1983, p. 219.