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MECHANISM OF THERMAL DECOMPOSITION OF THIOUREA DERIVATIVES

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The thermal decomposition of a series of compounds has been studied by thermogravimetry, mass spectrometry, nuclear magnetic resonance and elemental analysis. The combined use of mass spectrometry and thermogravimetry (MS and TG) in the analysis of these compounds has allowed characterization of the fragmentation pattern which was the objective of this research. The gaseous products, volatile condensed products and solid residues were identified by NMR and MS. Based on the product of thermal decomposition, the mechanism of thermal decomposition has been derived.

Keywords: *mass spectrometry, mechanism of decomposition, nuclear magnetic resonance, TG, thermal analysis, thermal decomposition*

Introduction

Identification of the gaseous products that are released in the degradation of a given compound could offer valuable information regarding its decomposition, permitting observation of each one of the stages or transitions determined by a thermogravimetry as well as the associated degradation process; based on this information, a mechanism of decomposition can be proposed.

Results from various studies carried out on thermal decomposition in order to determine the mechanism of decomposition have been published. In these cases, in addition to thermogravimetry and differential analysis, other types of thermal techniques and identifying techniques are combined, such as IR spectroscopy and mass spectroscopy [1–5]. Studying thermal behavior of a given compound using thermogravimetry and differential scanning calorimetry (DSC) reveals the compound's degradation profile, but these techniques are not adequate for determination of the decomposition products obtained during the degradation process. For the identification of said gaseous products, it is necessary to use other types of methods or techniques [6–8]. Mass spectra consist of a series of competitive and consecutive unimolecular fragmentations in conjunction with thermal decomposition which provide addictional data on the sample; they are very important in order to understand the chemical processes and mechanism of the fragmentation, since electron impact (EI) and thermal analysis (TA) fragmentation do not necessarily follow the same pattern [9].

In the method developed for the establishment of a mechanism of thermal decomposition or a series of thiourea derivatives, gaseous products released by the analyzed samples are collected and then identified by mass spectrometry and proton nuclear magnetic resonance.

Experimental

Materials

A series of thiourea compounds were used (series A, Table 1); they were synthetized in the pharmaceutical and organic chemistry department at the University of Navarra. The products are accompanied by identification assays which include: elemental analysis, IR, ^{1}H-NMR, HPLC, thermomicroscopy, MS and some additional observations. They have a high grade of purity because many of them were prepared for carrying out biological assays

Equipment and procedures

Thermogravimetry

The thermogravimetric studies are carried out with a thermobalance TGA-7 from Perkin-Elmer. The gases connected to the thermogravimetry equipment were nitrogen and air with a purity of 99.999%. The mass losses (3 mg samples) were measured in the temperature range of 100–450°C. The heating rate was 10°C min^{-1} in an inert atmosphere. This equipment was calibrated using alumel and nickel as thermally stable materials.

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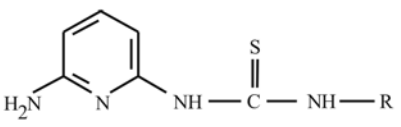
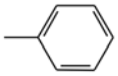
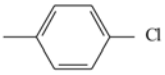
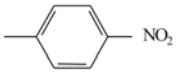
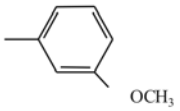
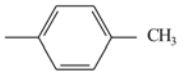
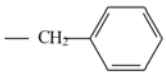
Table 1 Thiourea derivatives and their degradation temperatures



	R	T/°C
A-001		188.2 -193.2
A-002		195.3 -197.1
A-003		242.7 -245.2
A-004		208.8 -209.6
A-005		195.6 -196.2
A-006		223.4 -244.6

Scanning rate (heating rate): 10°C min^{-1}; sample masses: 3 mg

Nuclear magnetic resonance

The ^{1}H-NMR spectra have been obtained using a Bruker AC-200e (200 MHz) apparatus with the internal reference being tetramethylsilane at a concentration of 0.1 g mL^{-1} and with dimethylsulfoxide-d6 and chloroform d3 as solvents.

Mass spectral measurements and instruments

The mass spectra (MS-DIP) has been carried out using a Hewlett-Packard mass spectrometry 5988A with electron impact ionization at 70 eV. The samples were introduced by means of direct insertion probe (DIP). The instrument was calibrated using perfluorotributylamine as standard material.

Methods

After identifying the compounds under study, and in order to isolate and characterize their decomposition products, the following procedures were carried out:

- Introduction of the compounds in a sublimator or cold finger which is immersed in a sand bath at 200°C and with an internal feedwater circuit (10–15°C). Vacuum is not used. Samples are collected from different parts of the sublimator: sample deposited in the cold finger in crystalline form (S1), sample deposited on the inside walls of the exterior tube (S2) and sample of melted residue which remains at the base of the exterior tube (S3).

Analysis of each one of the fractions by mass spectrometry (MS-DIP) and nuclear magnetic resonance of the crystalline sample (NMR) are carried out.

- Thermogravimetric analysis of the compounds: vapors are collected at the gas outlet of the thermobalance oven by means of solid phase extraction, forcing the vapors from the thermobalance through a minicolumn C18 previously conditioned with methanol. Once the operation has finished, the substances retained in the minicolumn are extracted with 1 mL of methanol and then identified by means of mass spectrometry.

Results and discussion

Characterization of the compounds under study

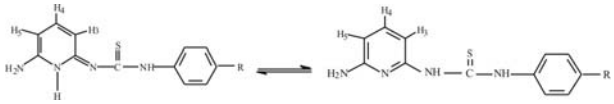


Fig. 1a Tautomeric equilibrium

^{1}H-NMR data of the compounds shows the presence of the following tautometry:

A singlet at δ between (according to *R*) 12.25 and 14.43 ppm (^{1}H) indicates that the compounds are in form I. The loss of aromaticness of the pyridine ring is confirmed by δ of the hydrogens H-3 and H-5 (6.06–6.39 ppm) and the hydrogen H-4 (7.20–7.68 ppm).

Identification of the most important fragments in mass spectrum of each compound (Tables 2–4). The pattern of fragmentation has been established by mass spectrometry (Fig. 1b):

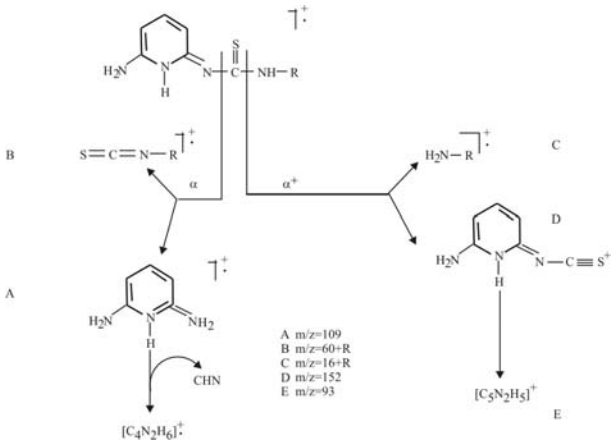


Fig. 1b Pattern of fragmentation of the derivatives from series A

Degradation temperatures and curves (Figs 2a–f) of thiourea derivatives

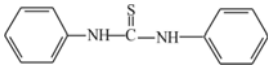
The decomposition temperatures of the thiourea derivatives are shown in the Table 1.

Identification of the decomposition vapors

Degradation of compound A-001 (Table 2)

- Identification of products obtained in the sublimator

Identification by mass spectrometry: the majority of the degradation vapors produced form a product identified as N,N'-diphenylthiourea (A-001/S1) (Table 5).



The melted residue at the base of the sublimator (A-001/S3) corresponds to a mixture of compound A-001 and other degradation products such as 2,6-diaminopyridine (*m*/*z*=109).

Identification by ^{1}H-NMR: ^{1}H-NMR of A-001/S1 shows an increase in the signals at δ between 7.03 and 7.34 ppm (benzene protons) and a singlet at δ 7.84 ppm (thioamide hydrogen). In A-001/S3, two doublets appear at δ 5.78 and 5.82 ppm (H-3 and H-5 of pyridine). By means of ^{1}H-NMR the presence of various degradation compounds derived from A-001 and which can coincide with the structures deduced from mass spectrometry can be justified.

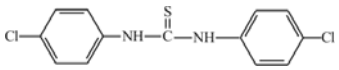
- Identification of vapors and residues obtained from the thermobalance

Mass spectrum of A-001/V1 (at the outlet of the TG) is the same as that obtained in A-001/S1 and corresponds to the dimer product, N,N'-diphenylthiourea. The results obtained indicate that upon being subjected to dynamic heating by thermogravimetry, the compound A-001 suffers a decomposition process which is similar to that produced upon introducing a sample in a sublimator in the previously described conditions, releasing the decomposition products indicated in previous section.

Degradation of compound A-002 (Table 2)

- Identification of products obtained in the sublimator

Identificaction by mass spectrometry: mass spectrum of a degradation product (in A-002/S1), indicates the chemical structure of N,N'-di-*p*-chlorophenylthiourea (Table 5).



Mass spectrum of A-002/S3 (sample at the base of the tube) indicates that this sample contains compound A-002 and other degradation products such as 2,6-diaminopyridine.

- Identification of the vapors and residues from the thermobalance

Mass spectrum of the sample A-002/V1 (vapors at the outlet of the TG) corresponds to the degradation product N,N'-di-*p*-chlorophenylthiourea. The dynamic assays carried out indicate the high volatility of this product (Fig. 3). The comparison between TG curves indicates that the thermal stability of compound N,N-di-*p*-chlorophenylthiourea (synthetized in the laboratory) is less than that of compound A-002; therefore, once the degradation product is formed in the melted mass, it is eliminated and degraded rapidly.

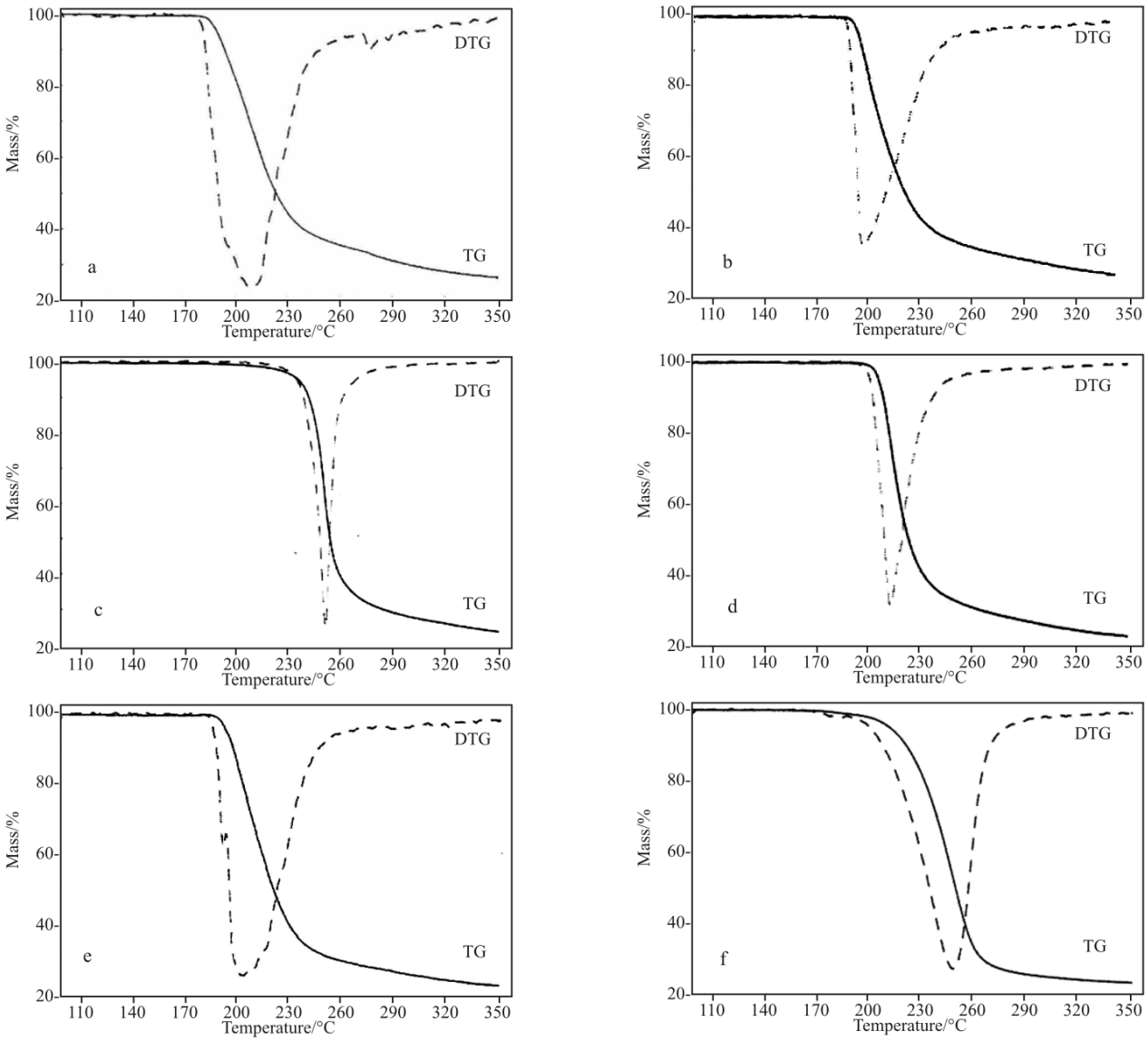


Fig. 2 TG and DTG curves at 10°C min^{-1} of compound a – A-001 at 3.67 mg, b – A-002 at 3.28 mg, c – A-003 at 3.19 mg, d – A-004 at 3.45 mg, e – A-005 at 3.38 mg anf f – A-006 at 3.55 mg

The mass spectrum of sample A-002/I1 (residue after isothermic scanning) indicates that a degradation product has been produced but instead of being N,N'-di-*p*-chlorophenylthiourea, the product is *p*-chloroaniline.

From the aforementioned data it can be concluded that in the degradation of compound A-002, a very volatile degradation compound, N,N'-di-*p*-chlorophenylthiourea is produced and breaks off from the sample at high speed. Fragmentations of the molecule are also produced and they give rise to other degradation products such as *p*-chloroaniline.

Degradation of compound A-003 (Table 3)

- Identification of the products obtained in the sublimator

Compound A-003 has a decomposition temperature by thermogravimety that is markedly superior to the rest of the compounds of the series (Table 1). The condensed vapors in the sublimator are collected, prolonging the heating process for h (the same behaviour occurs to compounds A-004 and A-006).

Differences with respect to the abundances of certain fragments are detected, such as $(C_6H_6N_3S)^+$ which indicates the presence of isocyanate of 6-amino-2-pyridyl (*m*/*z*=152.05).

Table 2 Fragments and relative abundances (expressed in %) of A-001 and A-002 compounds and their thermal degradation products

	A–001							A–002						
m/z	93.05	109.05	135.05	152.05	244.05	194.05	228.05	109.05	127.05	152.05	169.05	278.05	262.05	296.05
A	79.23	100.00	11.32	27.42	49.43*	–	–	100.00	27.46	51.74	8.74	55.25*	–	–
1. Samples obtained in the sublimator														
S1	100.00	15.39	11.97	0.56	–	15.45	36.87	47.91	100.00	7.55	29.00	–	18.15	12.22
S2	82.45	100.00	21.59	29.84	62.28	–	–							
S3	6.49	100.00	57.86	11.18	1.46	–	–	100.00	57.27	48.99	20.54	35.92	–	–
2. Samples obtained in the thermobalance														
V1	100.00	10.06	12.28	0.38	–	–	12.39	14.39	100.00	8.69	35.42	–	44.70	19.31
I	79.01	100.00	17.65	19.25	37.76	–	6.43	100.00	44.39	41.80	12.56	34.65	–	–
m/z (A-001): 93.05 $(C_6H_7N)^{+\cdot}$, 109.05 $(C_5H_7N_3)^{+\cdot}$, 135.05 $(C_7H_5NS)^{+\cdot}$, 152.05 $(C_6H_6N_3S)^{+}$, 244.05 $(C_{12}H_{12}N_4S)^{+\cdot}$, 194.05 $(C_{13}H_{10}N_2)^{+\cdot}$, 228.05 $(C_{13}H_{12}SN_2)^{+\cdot}$														
m/z (A-002): 109.05 $(C_5H_7N_3)^{+\cdot}$, 127.05 $(C_6H_6NCl)^{+\cdot}$, 152.05 $(C_6H_6N_3S)^{+}$, 169.05 $(C_7H_4NSCl)^{+\cdot}$, 278.05 $(C_{12}H_{11}N_4SCl)^{+\cdot}$, 262.05 $(C_{13}H_8N_2Cl_2)^{+\cdot}$, 296.05 $(C_{13}H_{10}N_2SCl_2)^{+\cdot}$														

*Molecular ion

S1: crystalline sample from the sublimator; S2: sample deposited on the tube wall; S3: sample of melted residue at the base of the tube; V1: vapors at the outlet of the TG; I: residue after isothermal scanning (A-001: at 180°C, 10 min (mass loss: 29.4%); A-002: at 187.5°C, 10 min (mass loss: 33.7%))

Table 3 Fragments and relative abundances (expressed in %) of A-003 and A-004 compounds and their thermal degradation products

	A-003							A-004						
m/z	93.05	109.05	138.05	152.05	180.05	255.05	289.05	109.05	123.05	152.05	165.05	274.05	254.05	288.05
A	67.41	100.00	18.24	45.70	12.54	23.61	24.68*	100.00	60.14	24.27	24.92	58.79*	–	–
1. Samples obtained in the sublimator														
S1	74.31	100.00	31.72	85.42	17.94	44.43	23.75	54.98	100.00	–	51.55	–	29.14	29.62
S2	42.65	100.00	32.88	55.82	21.01	22.80	18.37	52.75	100.00	11.51	55.38	18.24	24.01	25.89
S3	89.56	100.00	14.90	82.61	11.77	65.26	18.19							
2. Samples obtained in the thermobalance														
V1	74.19	100.00	35.40	69.79	35.53	34.55	34.44							
I1	68.91	100.00	21.86	53.13	14.72	34.41	24.67	100.00	43.80	29.79	13.87	69.47	–	–
I2	62.51	100.00	27.93	46.94	13.15	12.45	15.63	100.00	56.41	28.21	17.07	69.79	–	–
m/z (A-003): 93.05 $(C_6H_7N)^+$, 109.05 $(C_5H_7N_3)^+$, 138.05 $(C_6H_6N_2O_2)^{+\cdot}$, 152.05 $(C_6H_6N_3S)^+$, 180.05 $(C_7H_4N_2O_2S)^{+\cdot}$, 255.05 $(C_{12}H_9N_5O_2)^{+\cdot}$, 289.05 $(C_{12}H_{11}N_5O_2S)^{+\cdot}$														
m/z (A-004): 109.05 $(C_5H_7N_3)^{+\cdot}$, 123.05 $(C_7H_9NO)^+$, 152.05 $(C_6H_6N_3S)^+$, 165.05 $(C_8H_7NOS)^{+\cdot}$, 274.05 $(C_{13}H_{14}N_4OS)^{+\cdot}$, 254.05 $(C_{15}H_{14}N_2O_2)^{+\cdot}$, 288.05 $(C_{15}H_{16}N_2O_2S)^{+\cdot}$														

*Molecular ion

S1: crystalline sample from the sublimator; S2: sample deposited on the tube wall; S3: sample of melted residue at the base of the tube; V1: vapors at the outlet of the TG; I1: residue after isothermal scanning (A-003: mass loss: 10%; A-004: at 190.0°C (mass loss: 5%)); I2: residue after isothermal scanning (A-003: mass loss: 50%; A-004: at 195.0°C (mass loss: 5%))

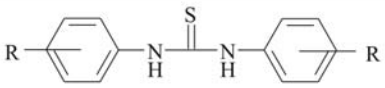
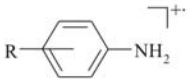
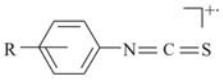
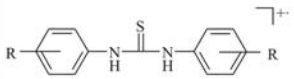
Table 4 Fragments and relative abundances (expressed in %) of A-005 and A-006 compounds and their thermal degradation products

	A-005							A-006						
m/z	107.05	109.05	149.05	152.05	258.05	222.05	256.05	91.05	106.05	109.05	152.05	225.05	258.05	256.05
A	54.37	100.00	14.23	23.71	47.12			88.92	41.55	100.00	30.67	41.02	69.58*	–
1. Samples obtained in the sublimator														
S1	100.00	25.13	12.31	1.58	4.64	28.06	55.87	79.19	100.00	12.88	2.89	4.54	11.72	47.65
S2	91.07	100.00	19.07	26.42	66.89	8.59	23.26	100.00	54.67	72.64	24.64	27.36	52.41	2.70
2. Samples obtained in the thermobalance														
V1								100.00	32.92	2.65	1.02	–	2.15	28.62
I1	48.84	100.00	12.06	26.89	63.60	–	–	100.00	50.26	99.34	38.77	47.28	80.79	–
I2	92.22	100.00	20.33	25.76	27.73	12.00	17.53							
m/z (A-003): 107.05 $(C_7H_9N)^{+\cdot}$, 109.05 $(C_5H_7N_3)^{+}$, 149.05 $(C_8H_7NS)^{+\cdot}$, 152.05 $(C_6H_6N_3S)^{+}$, 258.05 $(C_{13}H_{14}N_4S)^{+\cdot}$, 222.05 $(C_{15}H_{14}N_2)^{+\cdot}$, 256.05 $(C_{15}H_{16}N_2S)^{+\cdot}$														
m/z (A-004): 91.05 $(C_7H_7)^{+}$, 106.05 $(C_7H_8N)^{+\cdot}$, 109.05 $(C_5H_7N_3)^{+\cdot}$, 152.05 $(C_6H_6N_3S)^{+}$, 225.05 $(C_{13}H_{13}N_4)^{+}$, 258.05 $(C_{13}H_{14}N_4S)^{+\cdot}$, 256.05 $(C_{15}H_{16}N_2S)^{+\cdot}$														

*Molecular ion

S1: crystalline sample from the sublimator; S2: sample deposited on the tube wall; V1: vapors at the outlet of the TG; I1: residue after isothermal scanning (A-005: 170°C, 10 min (mass loss: 5%); A-006: at 195.0°C (mass loss: 21.6%)); I2: residue after isothermal scanning (A-005: at 180°C, 10 min (mass loss: 30%); A-004: at 195.0°C (mass loss: 5%))

Table 5 Fragmentation pathway by mass spectrometry of dimers formed in the decomposition process of compounds A-001 (*R*=H), A-002 (*R*=Cl), A-004 (*R*=OCH_3) and A-005 (*R*=CH_3)

Identified structures				
				
Structure	R	Ratio m/z		A/%
	R= H	m/z = 77.00	$(C_6H_5)^+$	35.14
	R = Cl (p)	m/z = 111.00	$(C_6H_4Cl)^+$	31.17
	R = OCH_3 (m)	-	-	-
	R = CH_3 (p)	-	-	-
	R= H	m/z = 93.00	$(C_6H_7N)^{+\cdot}$	100.00
	R = Cl (p)	m/z = 127.00	$(C_6H_6NCl)^{+\cdot}$	100.00
	R = OCH_3 (m)	m/z = 123.00	$(C_7H_9NO)^{+\cdot}$	-
	R = CH_3 (p)	m/z = 107.00	$(C_7H_9N)^{+\cdot}$	-
	R= H	m/z = 135.00	$(C_7H_5NS)^{+\cdot}$	11.97
	R = Cl (p)	m/z = 169.00	$(C_7H_4NSCl)^{+\cdot}$	12.45
	R = OCH_3 (m)	m/z = 165.00	$(C_8H_7NSO)^{+\cdot}$	-
	R = CH_3 (p)	m/z = 149.00	$(C_8H_7NS)^{+\cdot}$	-
	R= H	m/z = 194.00	$(C_{13}H_{10}N_2)^{+\cdot}$	15.45
	R = Cl (p)	m/z = 262.00	$(C_{13}H_8N_2Cl_2)^{+\cdot}$	7.06
	R = OCH_3 (m)	m/z = 254.00	$(C_{15}H_{14}N_2O_2)^{+\cdot}$	-
	R = CH_3 (p)	m/z = 222.00	$(C_{15}H_{14}N_2)^{+\cdot}$	-
	R= H	m/z = 228.00	$(C_{13}H_{12}N_2S)^{+\cdot}$	40.67
	R = Cl (p)	m/z = 296.00	$(C_{13}H_{10}N_2SCl_2)^{+\cdot}$	15.52
	R = OCH_3 (m)	m/z = 288.00	$(C_{15}H_{16}N_2SO_2)^{+\cdot}$	-
	R = CH_3 (p)	m/z = 256.00	$(C_{15}H_{16}N_2S)^{+\cdot}$	-

A(%): relative abundances in %

• Identification of the vapors emitted by the thermobalance

The compound A-003, upon heating, suffers an important sublimation (A-003/I1) along with a degradation of the compound (A-003/I2), generating degradation products such as isocyanate of 6-amino-2-pyridyl and isocyanate of *p*-nitrophenyl (A-003/V1).

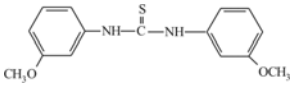
Studying the degradation vapors did not lead to the identification of the dimer N,N'-di-*p*-nitrophenylthiourea. Compound N,N'-di-*p*-nitrophenylthiourea synthetized in the laboratory presents a thermal stability which is inferior to that observed for compound A-003 (Fig. 4), so the temperature at which decomposition of compound A-003 begins is too high to permit formation of the compound N,N'-di-*p*-nitrophenylthiourea.

This different type of thermal behavior could be attributed to the presence of a NO_2 group in the compound structure. It appears that the strong electron-withdrawing character of the group produces an electronic distribution in the structure which makes it present specific characterization with regard to thermal decomposition.

Degradation of the compound A-004 (Table 3)

• Identification of the products obtained in the sublimator

Identification by mass spectrometry: a new dimerized degradation product N,N'-di-3-methoxyphenylthiourea is formed (Table 5), whose structure is as follows (appears mixed in A-004/S1 and A-004/S2):



Identification by ^{1}H-NMR: a signal at δ =13.30 ppm (hydrogen bonded to the nitrogen of pyridine) justifies the presence of compound A-004. The signals of hydrogens of the methoxyl group and the aromatic hydrogen signals, justifies the formation of N,N'-di-3-methoxyphenylthiourea.

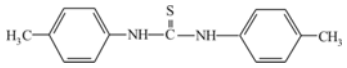
- Identification of residues and vapors emitted by the thermobalance

It can be observed that there are no great differences with compound A-004 (the degradation products are very volatile and once they are formed, they evaporate rapidly).

Degradation of compound A-005 (Table 4)

- Identification of the products obtained in the sublimator

The mass spectrum A-005/S1 shows signals of a product of degradation corresponding to the following structure (Table 5):



The sample on the tube wall (A-005/S2) is a mixture of A-005, of N,N'-di-*p*-methylphenylthiourea and of other degradation products such as *p*-methylaniline.

Identification by ^{1}H-NMR: A-005/S2 ^{1}H-NMR spectrum shows signals of compound A-005 together with other degradation compounds, N,N'-di-*p*-methylphenylthiourea and 2,6-diaminopyridine. The variation in the signals produced at δ=2.27 ppm (methyl group) and the presence of the signals of the hydrogens H-2', H-3', H-5' and H-6' of the substitution in *para* of the compound N,N'-di-*p*-methylphenylthiourea, along with the presence of signals of the hydrogens H-3 (δ=5.59 ppm), H-4 (δ=7.09 ppm) and H-5 (δ=5.63 ppm) of 2,6-diaminopyridine, justify the presence of the three compounds.

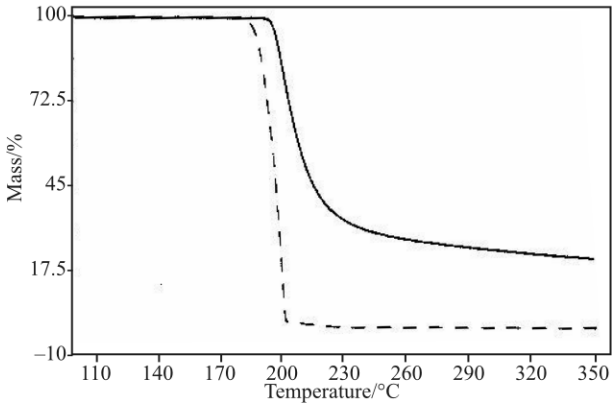


Fig. 3 TG curves of — – compound A-002 and - - - – dimer N,N'-di-*p*-chlorophenylthiourea at 20°C min^{-1}

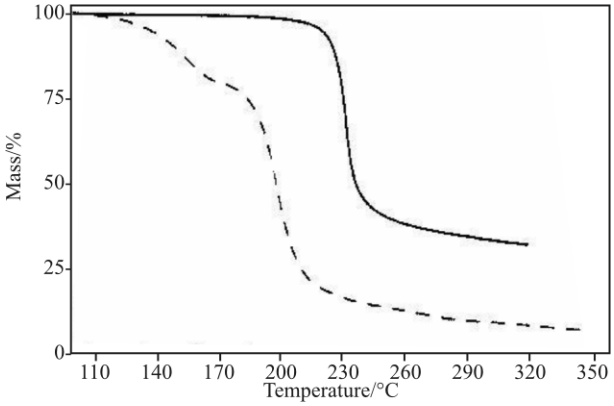


Fig. 4 TG curves of — – compound A-003 and - - - – dimer N,N'-di-*p*-nitrophenylthiourea at 10°C min^{-1}

- Identification of residues and vapors from the thermobalance

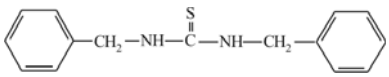
In the mass spectrum of A-005/I2 is observed an increase in the relative abundancy of the fragment at *m*/*z*=107.15, a decrease in the relative abundancy of the molecular ion and the presence of the molecular ion of the compound, N,N'-di-*p*-methylphenylthiourea.

Degradation of compound A-006 (Table 4)

- Identification of products obtained in the sublimator

Mass spectrometry of the sample A-006/S1 indicates the majority existence of N,N'-dibenzylthiourea (Table 6).

- Study of vapors and residues from the thermobalance



Mass spectrometry of the sample A-006/V1 indicates the majority presence of the degradation product N,N'-dibenzylthiourea and a small quantity of A-006.

The compound N,N'-dibenzylhtiourea has been synthetized in the laboratory in order to study its behavior with heat. The TG curve obtained presents a steep fall similar to that presented by compound A-006 (Fig. 5). Comparing the mass spectrum of the synthetized compound (*m*/*z*=91.05 (95.94%), 106.00 (100.05%) and 256.05 (21.33%)) with that obtained from the vapors collected at the end of the thermobalance (A-006/V1) it can be concluded that in

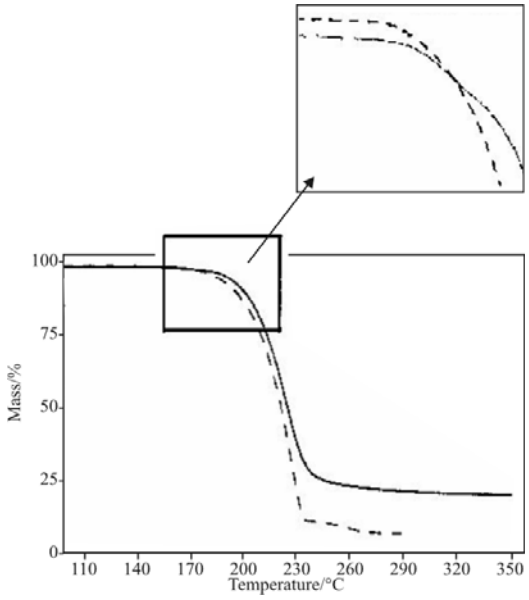


Fig. 5 TG curves of — – compound A-006 and - - - – dimer N,N'-dibenzylthiourea at 10°C min^{-1}

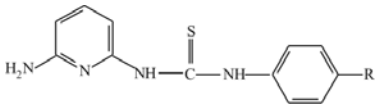
the thermal degradation of compound A-006 by thermogravimetry, the compound N,N'-dibenzylthiourea is produced in addition to other degradation products coming from the decomposition of the dimerized product, justifying the great relative abundance of the fragment with ratio *m*/*z*=91.05.

It is observed that formation of the dimer N,N'-dibenzylthiourea is slower due to the influence of the benzyl group and, in addition, the dimer compound is thermally more stable, producing a slower elimination than the degradation products.

Possibly, the slowest part of this degradation process could be due to the dehydrogenation α, β with respect to the aromatic ring of a good part of the sample (mass loss observed in the first transition of the TG curve, at 187°C approx., Fig. 2f) which generates a system π amply delocated of low energy, making the degradation of the compound slower.

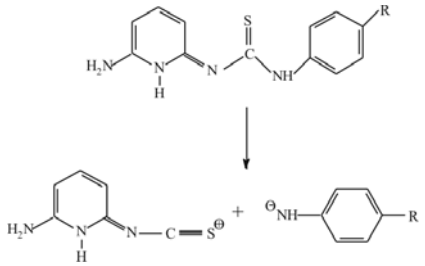
Determination of the mechanism of decomposition

A series of compounds have been studied; their general formula is:

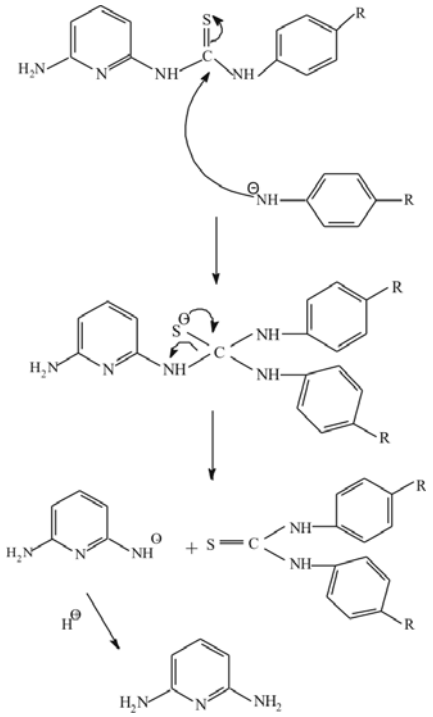


It has been spectroscopically demonstrated that these molecules exist in tautomeric equilibrium (Fig. 1a). Form I is the most abundant because the congugated system presents greater extension (in spite of the pyridinic ring having lost aromaticity) although, due to the tension of the ring, the orbital full of pyridinic nitrogen with the delocalized system, a partial overlapping is still maintained, while in form II, the same does not occur with the thiourea nitrogen because due to greater release of the open chain, it does not connect the π systems of thiourea and pyridine.

Thioureas easily fragment in α position with high relative abundancies in MS of resulting fragments. It is probable that the thermal degradation originates in these bonds, too:

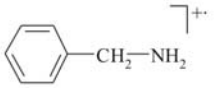
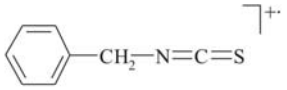
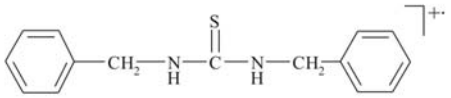


A non-alterated molecule in form II, due to the fact that it has a more positive thiocarbonylic carbon (it does not participate in the conjugation), suffers a nucleophilic attack:

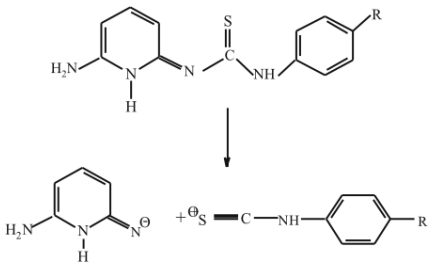


Both products are identified in high proportion in the final residue.

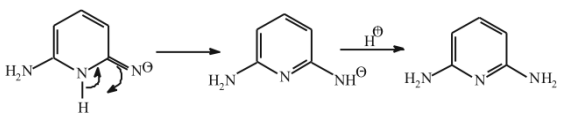
Table 6 Fragmentation pattern by mass spectrometry of dimer formated in the decomposition of compound A-006

Structure	Ratio m/z
	$(C_7H_7)^+$ $m/z = 91.00$
	$(C_7H_9N)^{+\cdot}$ $m/z = 107.00$
	$(C_8H_7NS)^{+\cdot}$ $m/z = 149.00$
	$(C_{15}H_{14}N_2)^{+\cdot}$ $m/z = 222.00$
	$(C_{15}H_{16}N_2S)^{+\cdot}$ $m/z = 256.05$

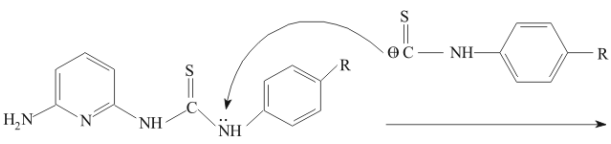
The heterolytic break at the other side of the thiocarbonyl has also been considered, producing the following species:

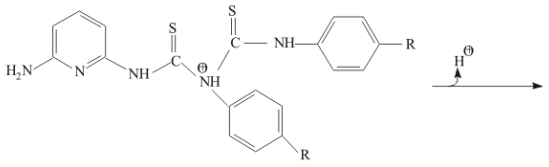


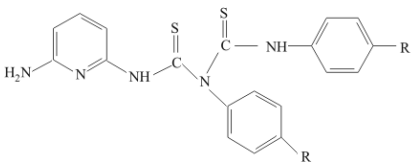
From one of the above, the evolution to follow is easy to foresee:



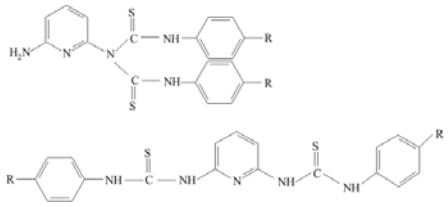
Especially, taking into account its great stability and the fact that it is not combined with other fragments in the analysis of the final residue, but rather as an independent product and in considerable abundancy:



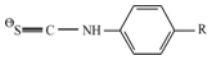




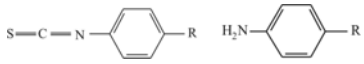
- In this process the indicated exit of a proton is more probable than the pyridinic thioacyl that would lead the dimer detected in the residue.
- any other position of nucleophilic attack, nitrogens substituted in the pyridinic ring, carries the following compounds:



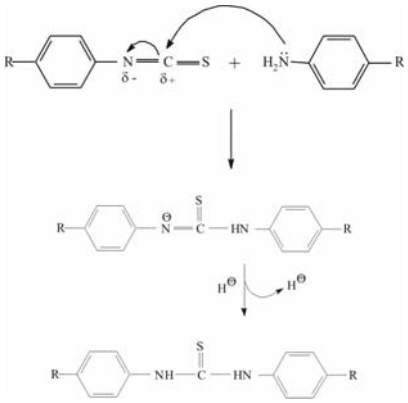
that are not identified in the final residue because they are not formed or because they suffer thermal decomposition once again and therefore the species:



possibly evolves the thioisocyanate or the amine in view of the stability of these fragments in mass spectrometry:



These compounds, at the same time, result reactive among them, possibly originating the dimer through another route:



Conclusions

In this work, research was carried out on a series of compounds derived from thiourea. A comparative study of the fragmentation by MS and decomposition by TG shows similarity. This research work concluded that both MS and TG are complimentary techniques and can be used to declare the thermal decomposition of these compounds on heating; the mass spectra help the selection of their suitable thermal decomposition mechanisms.

The compounds studied present very specific thermal decomposition parameters which permit the proposal of a tentative decomposition mechanism based on the degradation products found, the fragmentation patterns obtained by mass spectrometry and reference literature data regarding degradation of thioureas [10].

The identification of vapors and decomposition products resulting from the degradation process of the compounds show that the products formed respond to the structure R–NH–CS–NH–R, together with other compounds resulting from nitrogen-carbon fragmentation of the thiourea. Some authors have also described the formation of this type of products in degradation processes from certain organic compounds [11, 12].

The information gathered on these compounds relates the stages or transitions that are observed in the thermogravimetric curves with the degradation processes that occur in each compound. The first peak, the first 'shoulder' that appears in the DTG curve, corresponds to the formation of dimerized degradation products. Next, given the high volatility, a large release of this product is generated. Lastly, the successive transitions that are recorded in the last part of the DTG curve correspond to degradation of the dimer formed and other degradation products from the compound under study.

The presence of products of decomposition with the structure R–NH–CS–NH–R in the vapors of decomposition of the thiourea derivatives and the rapid fall observed in their TG curves, suggests that the dimers formed are rapidly eliminated from the melted mass of the compound under study.

The influence of certain substituents on the thermal behavior of the compounds of the series has been observed. The presence of a benzyl group modifies the degradation behavior, slowing it down, because the dimer compound is thermally more stable. However, the degradation mechanism follows the same pattern previously indicated. The presence of a nitro group in the structure modifies the proposed degradation mechanism and it is not possible to identify the desired dimer, N,N'-di-*p*-nitrophenylthiourea.

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