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THERMAL AND KINETIC STUDIES ON THE STABILITY OF SOME THIOUREIDO-SULFONAMIDE DERIVATIVES

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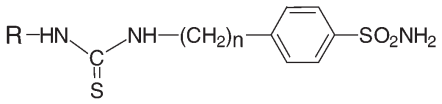
Abstract

The kinetic and thermal behaviour for the following compounds:



where: *R*=phenyl, allyl; *n*=0, 1, 2 was studied by TG and DTA techniques.

The compounds decompose in many steps; the last one corresponding to the burning of $H_2N–S–C_6H_4–C_6H_4–S–NH_2$ occurs with comparable reaction rates.

Keywords: non-isothermal, thermal decomposition, thioureido-sulfonamide

Introduction

The sulfonamido compounds are biologically active molecules. Their importance is determined by the potencial chemotherapeutic effect. Most investigations showed that the complexation between transitional ions and one of this type of compounds leads to a dramatically increase of biologically-active properties [1, 2].

Thermal analysis is an appropriate method for the characterization of this type of complexes, but, firstly, it is necessary to elucidate the thermal behaviour of the uncomplexed potential ligand. Thus, we describe both a thermal study on the stability of some thioureido-sulfonamides and a kinetic study of some singulary steps of decomposition.

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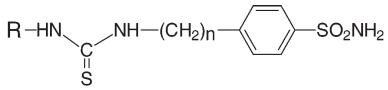
Experimental

Equipment and methods of working experimental data

The heating curves were recorded in static air atmosphere using a Q-1500D (Paulik, Paulik, Erdey) – MOM Budapest, derivatograph in the temperature range 25–700°C at various heating rates (β) between 2.5 and 5 K min^{-1}. DTA curves were recorded using Al_2O_3 as reference compound. Amounts of 90–100 mg of substance were used for the samples. Experimental data were processed with the computer program VERSATILE [3, 4]. Kinetic parameter values were obtained using the integral methods Coats–Redfern [5], Flynn–Wall for constant heating rate [6, 7] and Coats–Redfern modified by Urbanovici and Segal [8].

Samples

The following compounds of the general formula:



listed in Table 1 were used.

Table 1 List of the investigated compounds

Nr	*R*	*n*	Name
1	phenyl	0	N-(4-aminosulfonylphenyl)-N'-phenyl-thiourea
2	phenyl	1	N-(4-aminosulfonylphenylmethyl)-N'-phenyl-thiourea
3	phenyl	2	N-(4-aminosulfonylphenylethyl)-N'-phenyl-thiourea
4	allyl	0	N-(4-aminosulfonylphenyl)-N'-allyl-thiourea
5	allyl	1	N-(4-aminosulfonylphenylmethyl)-N'-allyl-thiourea
6	allyl	2	N-(4-aminosulfonylphenylethyl)-N'-allyl-thiourea

Synthesis and structural characterization of these compounds were reported in a previous paper [1].

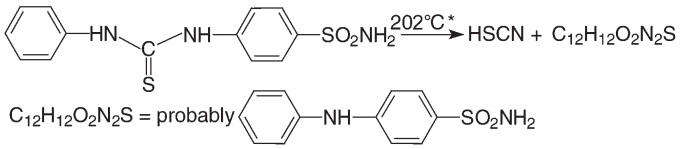
Results and discussions

N-(4-Aminosulfonylphenyl)-N'-phenyl-thiourea (β=2.5 K min^{-1})

TG curve shows that the melting of this compound (201–202°C) occurs in the same time with the beginning of the decomposition.

There are 4 decomposition steps, which can be assigned to the following reactions, according to their mass loss:

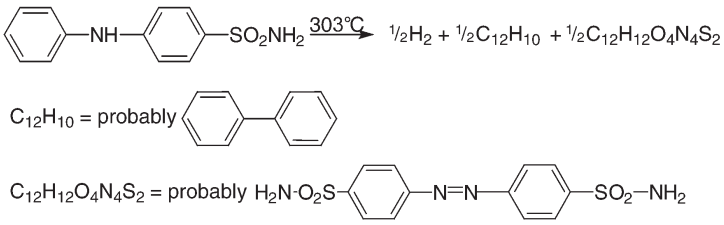
I.



In this step, the mass loss is:

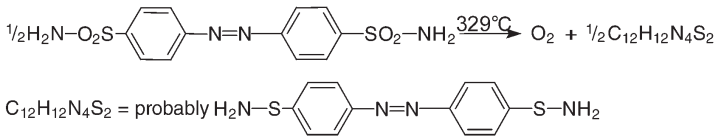
$\Delta m_{exp.}$=20.52%; $\Delta m_{calc.}$=19.22%

II.



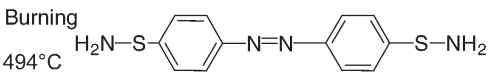
Mass loss: $\Delta m_{exp.}$=23.87%; $\Delta m_{calc.}$=25.08%

III.



Mass loss: $\Delta m_{exp.}$=10.47%; $\Delta m_{calc.}$=10.42%

IV.



Mass loss: $\Delta m_{exp.}$=44.4%; $\Delta m_{calc.}$=44.95%

The TG curve and the calculated kinetic parameter values for this last step, representing the burning of the fragment described above, are:

*All temperatures indicated on the arrows correspond to the maximum reaction rate.

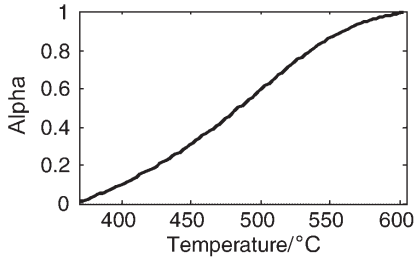


Fig. 1 TG curve for the IVth step of decomposition of N-(4-aminosulfonylphenyl)-N'-phenyl-thiourea

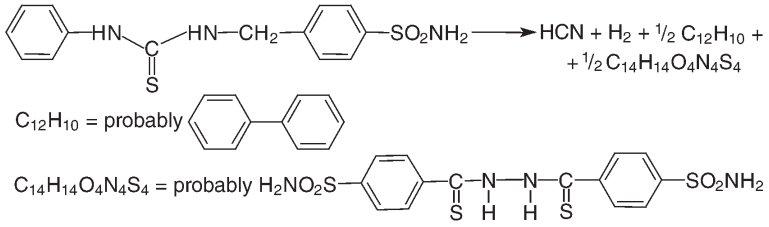
Table 2 Kinetic parameter values for the IVth step of decomposition of N-(4-aminosulfonyl-phenyl)-N'-phenyl-thiourea

Method	Coats–Redfern	Flynn–Wall	Urbanovici–Segal
Preexponential factor/s^{-1}	$5.24 \cdot 10^3$	$1.32 \cdot 10^4$	$8.43 \cdot 10^3$
Activation energy/kJ mol^{-1}	99.7	102.0	101.9
Reaction order	1.3	1.2	1.3
Correlation coefficient	–0.9797	–0.9842	–0.9804

N-(4-Aminosulfonylphenylmethyl)-N'-phenyl-thiourea (β*=2.5 K min^{-1})*

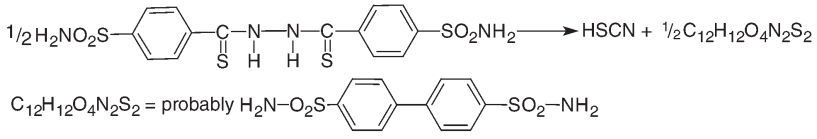
Decomposition process starts in the same time with melting (215–216°C):

I.



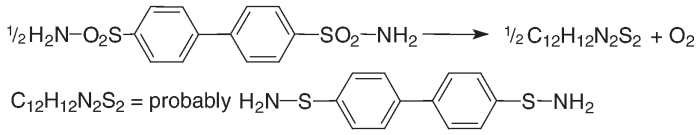
Mass loss: $\Delta m_{exp.}$=32.43%; $\Delta m_{calc.}$=33.02%

II.



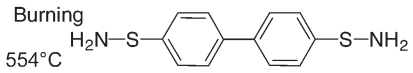
Mass loss: $\Delta m_{exp.}$=18.83%; $\Delta m_{calc.}$=18.38%

III.



Mass loss: $\Delta m_{exp.}$=9.41%; $\Delta m_{calc.}$=9.97%

IV.



Mass loss: $\Delta m_{exp.}$=38.70%; $\Delta m_{calc.}$=38.63%

The TG curve for this last decomposition step is shown in Fig. 2.

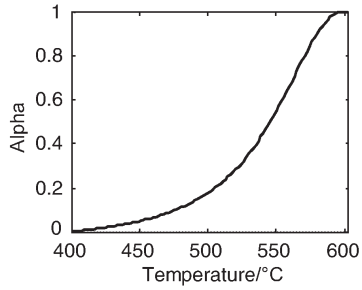


Fig. 2 TG curve for the IVth step of decomposition of N-(4-aminosulfonylmethyl-phenyl)-N'-phenyl-thiourea

For the last step, the burning, kinetic parameter values are:

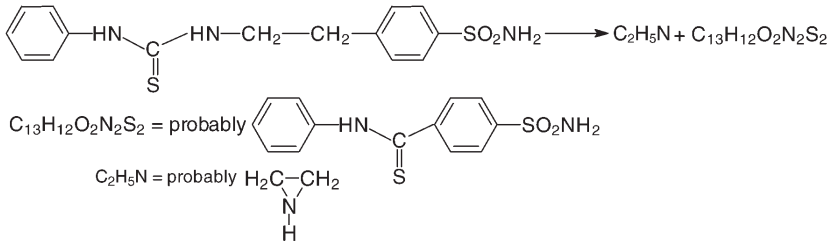
Table 3 Kinetic parameter values for the IVth decomposition step of N-(4-aminosulfonylphenyl-methyl)-N'-phenyl-thiourea

Method	Coats–Redfern	Flynn–Wall	Urbanovici–Segal
Preexponential factor/s^{-1}	$1.37 \cdot 10^5$	$2.61 \cdot 10^5$	$2.13 \cdot 10^5$
Activation energy/kJ mol^{-1}	130.2	132.2	132.5
Reaction order	0.7	0.6	0.7
Correlation coefficient	–0.9854	–0.9913	–0.9898

N-(4-aminosulfonylphenylethyl)-N'-phenyl-thiourea (β=5 K min^{-1})

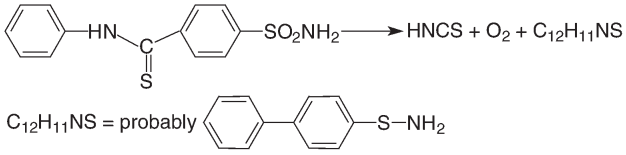
For this compound, decomposition begins in solid state, before melting (185–187°C):

I.



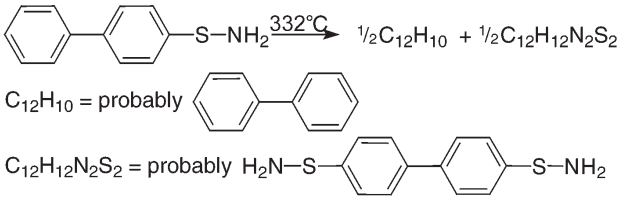
Mass loss: $\Delta m_{exp.}$=12.56%; $\Delta m_{calc.}$=12.84%

II.



Mass loss: $\Delta m_{exp.}$=29.42%; $\Delta m_{calc.}$=27.16%

III.



Mass loss: $\Delta m_{exp.}$=24.51%; $\Delta m_{calc.}$=22.99%

The TG curve for this decomposition step is presented in Fig. 3.

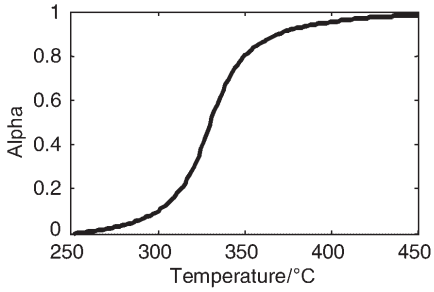


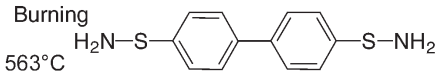
Fig. 3 TG curve for the I[st] step of decomposition of N-(4-aminosulfonylethylphenyl)-N'-phenyl-thiourea

Kinetic parameter values for this step are:

Table 4 Kinetic parameter values for the III[rd] step of decomposition of N-(4-aminosulfonyl-phenylethyl)-N'-phenyl-thiourea

Method	Coats–Redfern	Flynn–Wall	Urbanovici–Segal
Preexponential factor/s^{-1}	$9.15 \cdot 10^{13}$	$2.13 \cdot 10^{13}$	$2.73 \cdot 10^{13}$
Activation energy/kJ mol^{-1}	187.1	180.2	181.3
Reaction order	2.3	2.2	2.2
Correlation coefficient	–0.9940	–0.9946	–0.9939

IV.



Mass loss: $\Delta m_{exp.}$=35.34%; $\Delta m_{calc.}$=37.01%
The TG curve for this last decomposition step is:

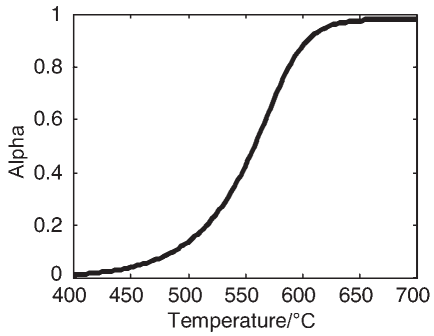


Fig. 4 TG curve for the IV[th] step of decomposition of N-(4-aminosulfonylethyl-phenyl)-N'-phenyl-thiourea

For this last step, kinetic parameter values are:

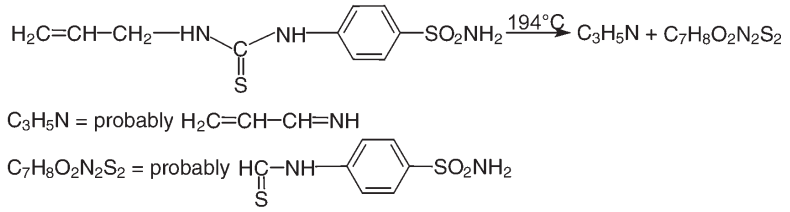
Table 5 Kinetic parameter values for the IV[th] step of decomposition of N-(4-aminosulfonyl-phenylethyl)-N'-phenyl-thiourea

Method	Coats–Redfern	Flynn–Wall	Urbanovici–Segal
Preexponential factor/s^{-1}	$4.92 \cdot 10^{5}$	$1.82 \cdot 10^{6}$	$7.11 \cdot 10^{5}$
Activation energy/kJ mol^{-1}	134.6	140.8	136.5
Reaction order	1.3	1.3	1.3
Correlation coefficient	–0.9941	–0.9951	–0.9945

N-(4-aminosulfonylphenyl)-N'-allyl-thiourea (β=5 K min^{-1})

In this case, the process of decomposition starts before melting (181–183°C):

I.



Mass loss: $\Delta m_{exp.}$=18.79%; $\Delta m_{calc.}$=20.32%

The TG curve and the kinetic parameter values are shown below:

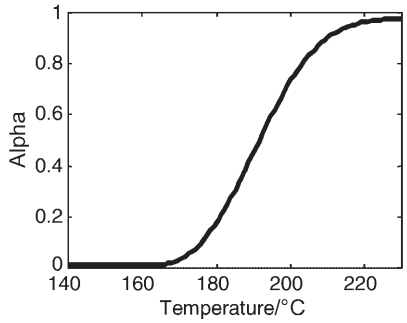
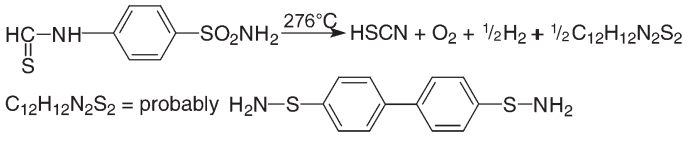


Fig. 5 TG curve for the Ist step of decomposition of N-(4-aminosulfonylphenyl)-N'-allyl-thiourea

Table 6 Kinetic parameter values for the Ist step of decomposition of N-(4-aminosulfonyl-phenyl)-N'-allyl-thiourea

Method	Coats–Redfern	Flynn–Wall	Urbanovici–Segal
Preexponential factor/s^{-1}	$9.20 \cdot 10^{17}$	$1.68 \cdot 10^{17}$	$3.92 \cdot 10^{17}$
Activation energy/kJ mol^{-1}	179.0	172.7	175.8
Reaction order	1.8	1.7	1.7
Correlation coefficient	–0.9839	–0.9851	–0.9848

II.



Mass loss: $\Delta m_{exp.}$=35.14%; $\Delta m_{calc.}$=33.95%

For this step, the TG curve and the kinetic parameter values are:

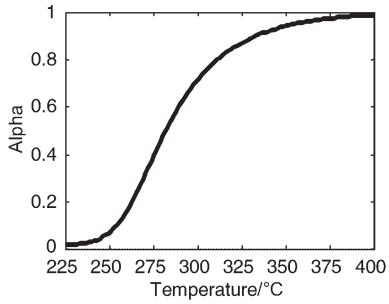
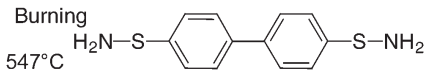


Fig. 6 TG curve for the II[nd] step of decomposition of N-(4-aminosulfonylphenyl)-N'-allyl-thiourea

Table 7 Kinetic parameter values for the II[nd] step of decomposition of N-(4-aminosulfonyl-phenyl)-N'-allyl-thiourea

Method	Coats–Redfern	Flynn–Wall	Urbanovici–Segal
Preexponential factor/s^{-1}	$9.04 \cdot 10^{12}$	$1.20 \cdot 10^{13}$	$1.61 \cdot 10^{13}$
Activation energy/kJ mol^{-1}	162.2	163.3	164.6
Reaction order	2.4	2.4	2.4
Correlation coefficient	–0.9918	–0.9927	–0.9913

III.



Mass loss: $\Delta m_{exp.}$=42.49%; $\Delta m_{calc.}$=45.76%
For this step, the TG curve and the kinetic parameter values are:

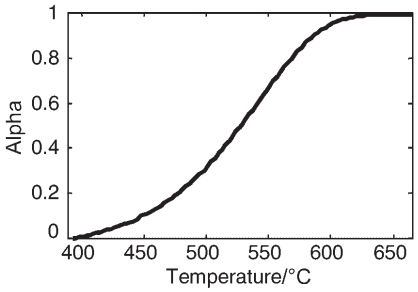


Fig. 7 TG curve for the III[rd] step of decomposition of N-(4-aminosulfonylphenyl)-N'-allyl-thiourea

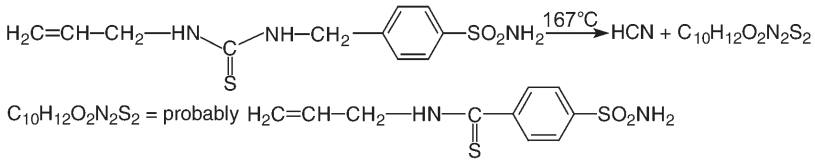
Table 8 Kinetic parameter values for the III[rd] step of decomposition of N-(4-aminosulfonyl-phenyl)-N'-allyl-thiourea

Method	Coats–Redfern	Flynn–Wall	Urbanovici–Segal
Preexponential factor/s^{-1}	$3.58 \cdot 10^5$	$1.38 \cdot 10^5$	$1.54 \cdot 10^6$
Activation energy/kJ mol^{-1}	127.9	134.0	136.0
Reaction order	1.3	1.3	1.4
Correlation coefficient	–0.9948	–0.9958	–0.9947

N-(4-aminosulfonylphenylmethyl)-N'-allyl-thiourea (β=2.5 K min^{-1})

The decomposition process starts in solid state; during melting (167–169°C) the reaction rate decreases probably due to a local cooling process because of the endothermic effect of melting. The amount of compound decomposed in solid state represents only 3.37% of the total amount. This led to the evaluation of the kinetic parameter values for the liquid state decomposition process.

I.



Mass loss: $\Delta m_{exp.}$=9.42; $\Delta m_{calc.}$=9.47%

For this step, the TG curve and the kinetic parameter values are:

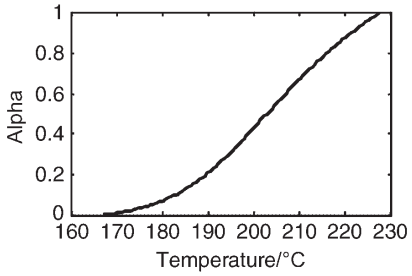


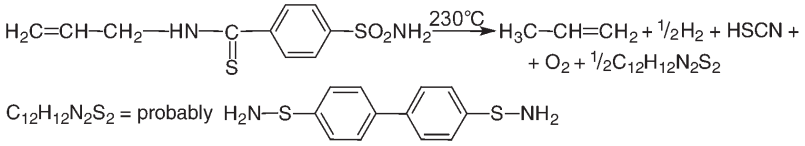
Fig. 8 TG curve for the I[st] step of decomposition of N-(4-aminosulfonylmethyl-phenyl)-N'-allyl-thiourea

Table 9 Kinetic parameter values for the Ist step of decomposition of N-(4-aminosulfonylphenyl-methyl)-N'-allyl-thiourea

Method	Coats–Redfern	Flynn–Wall	Urbanovici–Segal
Preexponential factor/s^{-1}	$2.36 \cdot 10^{22}$	$1.11 \cdot 10^{22}$	$1.17 \cdot 10^{22}$
Activation energy/kJ mol^{-1}	224.3	220.6	221.6
Reaction order	2.1	2.1	2.0
Correlation coefficient	–0.9908	–0.9914	–0.9904

The quite high values of the kinetic parameters indicate the complex character of this liquid phase decomposition.

II.



Mass loss: $\Delta m_{exp.}$=45.55%; $\Delta m_{calc.}$=47.02%

For this step, the TG curve and the kinetic parameter values are:

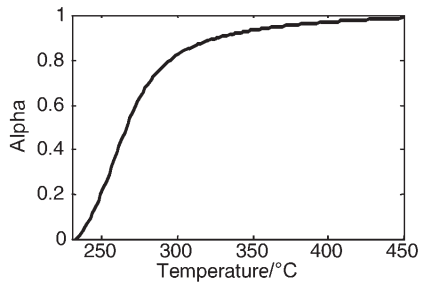
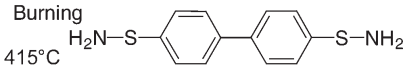


Fig. 9 TG curve for the IInd step of decomposition of N-(4-aminosulfonylmethyl-phenyl)-N'-allyl-thiourea

Table 10 Kinetic parameter values for the IInd step of decomposition of N-(4-aminosulfonyl-phenylmethyl)-N'-allyl-thiourea

Method	Coats–Redfern	Flynn–Wall	Urbanovici–Segal
Preexponential factor/s^{-1}	$9.83 \cdot 10^{12}$	$1.32 \cdot 10^{13}$	$1.96 \cdot 10^{13}$
Activation energy/kJ mol^{-1}	160.8	161.9	163.6
Reaction order	2.9	2.9	2.9
Correlation coefficient	–0.9749	–0.9778	–0.9748

III.



Mass loss: $\Delta m_{exp.}$=43.46%; $\Delta m_{calc.}$=43.51%

For this step, the TG curve and the kinetic parameter values are:

Table 11 Kinetic parameter values for the III[rd] step of decomposition of N-(4-aminosulfonyl-phenylmethyl)-N'-allyl-thiourea

Method	Coats–Redfern	Flynn–Wall	Urbanovici–Segal
Preexponential factor/s^{-1}	$1.25 \cdot 10^1$	$1.46 \cdot 10^2$	$3.28 \cdot 10^1$
Activation energy/kJ mol^{-1}	78.5	88.3	83.7
Reaction order	0.9	0.9	1.0
Correlation coefficient	–0.9857	–0.9901	–0.9861

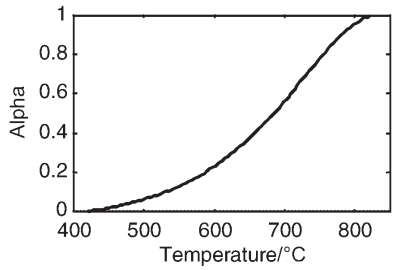
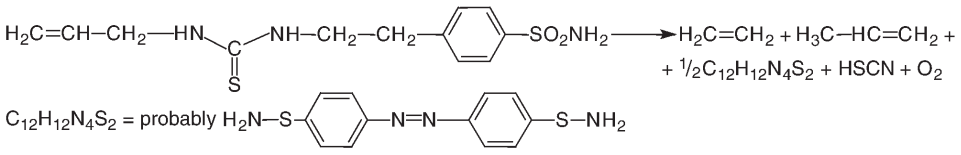


Fig. 10 TG curve for the III[rd] step of decomposition of N-(4-aminosulfonylmethyl-phenyl)-N'-allyl-thiourea

N-(4-aminosulfonylphenylethyl)-N'-allyl-thiourea (β=5 K min^{-1})

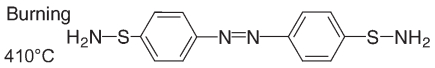
This compound decomposes after melting (148–150°C):

I.



Mass loss: $\Delta m_{exp.}$=53.93%; $\Delta m_{calc.}$=53.85%

II.



Mass loss: $\Delta m_{exp.}$=46.60%; $\Delta m_{calc.}$=46.15%
TG curves and kinetic parameter values are:

Table 12 Kinetic parameter values for the II[nd] step of decomposition of N-(4-aminosulfonyl-phenylethyl)-N'-allyl-thiourea

Method	Coats–Redfern	Flynn–Wall	Urbanovici–Segal
Preexponential factor/s^{-1}	$7.31 \cdot 10^3$	$3.83 \cdot 10^4$	$1.13 \cdot 10^4$
Activation energy/kJ mol^{-1}	113.6	120.9	115.7
Reaction order	1.0	1.0	1.0
Correlation coefficient	–0.9969	–0.9976	–0.9968

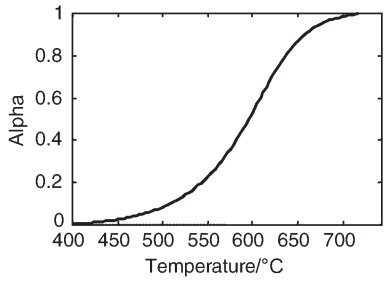


Fig. 11 TG curve for the II[nd] step of decomposition of N-(4-aminosulfonylethyl-phenyl)-N'-allyl-thiourea

The final steps, representing the burning of the $H_2N–S–C_6H_4–C_6H_4–S–NH_2$ fragment, occur smoothly in a relatively large temperature-range thus being kinetically workable. For these steps a compensation effect was observed between the values of the preexponential factor and the activation energy, the calculated values for the rate constant at 500°C exhibiting relatively close values:

Table 13 Kinetic parameter values for the steps that represent the burning of $H_2N–S–C_6H_4–C_6H_4–S–NH_2$: (Kinetic constants were calculated with the preexponential factors and the activation energies obtained by Coats–Redfern method)

Compound number	A/s^{-1}	E_a/kJ mol^{-1}	K_{773K}/s^{-1}	ΔG^*/kJ mol^{-1}	ΔS^*/ J mol^{-1} K^{-1}
2	$2.14 \cdot 10^5$	132.5	$2.16 \cdot 10^{-4}$	249.0	–150.8
3	$7.11 \cdot 10^5$	136.5	$3.89 \cdot 10^{-4}$	245.3	–140.8
4	$1.54 \cdot 10^6$	136.0	$8.10 \cdot 10^{-4}$	239.8	–134.4
5	$3.28 \cdot 10^1$	83.7	$6.18 \cdot 10^{-4}$	256.6	–223.7

The close values of the k_{773} are probably due to the oxidation of the same molecular fragment namely $H_2N–S–C_6H_4–C_6H_4–S–NH_2$.

The values for the activation entropy were calculated considering the activation energy equal to the activation enthalpy.

The strange negative values obtained for the activation entropy may be due to the structural ordering effect of O_2 on the burning reaction's transition state.

The proposed fragmentation schemes are in agreement with the following literature results:

1. Investigating the thermal decomposition of copper(I) thiocarbamide chloride hemihydrate, Krunks *et al.* [9] shows in the evolved gases the presence of HSCN as a result from the thiourea's thermal decomposition process.

2. Studying the thermal behaviour of some copper-acetazolamide (5-acetamido-1,3,4-thiadiazole-2-sulfonamide) complexes, Ferrer *et al.* [10] shows that the ligand degradation occurs with the disparition of the IR absorptions of carbonyl and sulfonyl groups, and, for the final step, the sulfur from the copper sulfate originate not only from oxidation of the thiadiazole ring but also directly from the sulfonamido group.

Conclusions

Investigation on the thermal stability of some thioureido-sulfonamide derivatives was carried out using a Q-1500D derivatograph.

The decomposition steps were established.

For the kinetically workable steps, the non-isothermal kinetic parameters were evaluated.

Similar reactions like burning are characterized by relatively close values of the free energy of activation.

The activation parameters exhibit an apparent compensation effect.

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