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Study on thermal behavior of some new diazoaminoderivatives

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Abstract

In the current paper three new diazoaminoderivatives are characterized by TG-DTG-DTA thermal methods in order to investigate the structure-thermostability-degradation mechanism correlation. The results of thermal analysis are indicative of a complex degradation mechanism which is characteristic of every sample, some similarities reflecting the structure influence being also noticed.

The thermostability series of the compounds under study is correlated to their structure.

The quantitative analysis by TG-DTG afforded the elucidation of some aspects of the thermal degradation mechanism. The melting points of the samples estimated from DTA and by the Boetius method were in good agreement. The initial degradation temperatures resulting from TG-DTG-DTA led to the estimation of the temperature range of using and storing these compounds which is an useful information if their possible practical applications and of some derivatives as herbicides, plant growth stimulators, fungicides, acaricides are taken into account. Apart from this, the presence of the azo group in the structure of these new compounds could make possible some useful applications for dying of proteic fibers.

Keywords: diazoaminoderivatives thermal analysis (TG-DTG-DTA), thermostability, action mechanism.

Introduction

Among the various classes of chemical compounds studied in recent times the aryloxyalcancarboxylic acids and their derivatives are particularly important for their herbicidal and auxinic action which has been knowing for long time. [1,2]

By introducing a sulphonamidic group in the structure of the phenoxyacetic, chlorophenoxyacetic, crezoxyacetic, xylenoxyacetic and phenoxy- the auxinic and herbicidal actions of these derivatives were much improved along with the absence of the toxic residues and with very low tocicity to human beings and mammalians[1-9]

By carrying on our previous studies in this field [10,11], the present paper is devoted to the synthesis and thermal characterization by TG-DTG-DTA thermal methods [10-15] of three new diazoaminoderivatives,1-(3-{2-[4-(aminomethyl)phenoxy]ethyl}triaz-1-enyl)-2-naphthol **(1),** 8-(3-{2-[2-(aminomethyl)-4-chlorophenoxy]ethyl}triaz-1-enyl)-2-hydroxy-1-naphthoic acid **(2),** 5-(3-{2-[4-(aminomethyl)-2-chlorophenoxy]ethyl}triaz-1-enyl)-2-hydroxybenzoic acid **(3)**, under nitrogen atmosphere, in order to follow the structure-thermostability-degradation mechanism correlation.

The structure of the newly synthesized derivatives could make them suitable for using in the agriculture and the textile industry as pesticides and azo dyes, respectively.

The characterization by thermal methods reveals the temperature range where the compounds under study may be used and stored and the thermostability series is correlated with their chemical structure and confirmed by the values of the apparent activation energies of the first process of the thermal degradation. The quantitative analysis by TG-DTG under nitrogen atmosphere afforded a discussion on the thermal degradation mechanism.
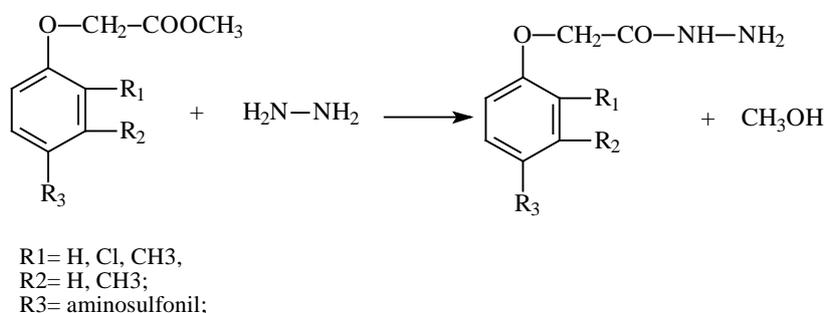
The compounds under study were found to suffer a thermal degradation into two stages, the first one being the most significant. The quantitative analysis by TG-DTG indicates that the first chemical process in the first stage till the temperature corresponding to the inflexion consists in the elimination of the NH_2-SO_2- group in every investigated compound followed by processes of specific degradation which is also dependent on the nature of the substitutes in their structures.

The kinetic parameters, n and Ea, estimated by two methods, [16,17], confirm the first process to be the breaking of similar bonds since the reaction order is the same, n=1 and the apparent activation energy is slightly influenced by the substitutes in the close vicinity. The melting temperatures estimated by both DTA [18-20] under nitrogen atmosphere and Boetius method were in good agreement.

Experimental

Synthesis of diazoaminoderivatives

The syntheses of dizoaminoderivatives were carried out into two stages, beginning with the synthesis of the sulphonamidated phenoxyacetic acid hydrazides according to the following reaction:

O—CH$_2$—COOCH$_3$ ... R$_1$, R$_2$, R$_3$ ... + H$_2$N—NH$_2$ → O—CH$_2$—CO—NH—NH$_2$ ... R$_1$, R$_2$, R$_3$ ... + CH$_3$OH

R1= H, Cl, CH3,
R2= H, CH3;
R3= aminosulfonil;

Scheme 1. Syntheses of hydrazides

In the second stage, the above mentioned hydrazides were submitted to the diazotization reaction followed by couplings with the following components: β-naphthol, BON acid, salicylic acid.
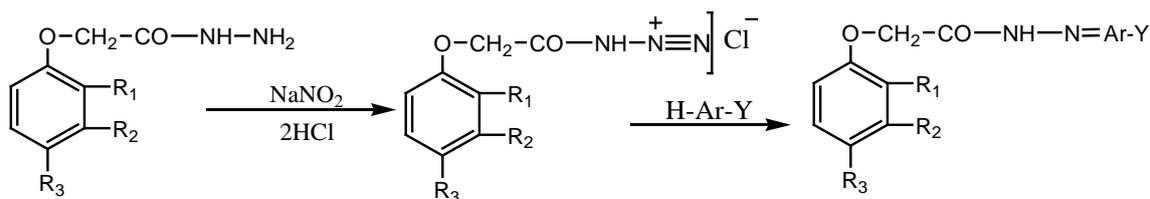
R_1= -H, -SO$_2$-NH$_2$, -Cl;
R_2= -H;
R_3= -Cl, -SO$_2$-NH$_2$;

Scheme 2. Syntheses of diazoaminoderivatives

The synthesis optimum conditions as well as the elemental analysis data and the NMR spectral measurement confirmed the formation of the corresponding diazoaminoderivatives. The mention has to be made that these compounds were separated with acetone as a solvent, $T_{b} = 56^0C$, evaporation temperature.

In scheme 3 the structures of the obtained diazoaminoderivatives, their chemical formulae, IUPAC denominations, molecular weights, and melting points measured by the Boetius method are given.
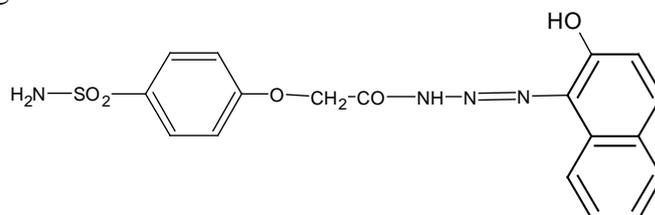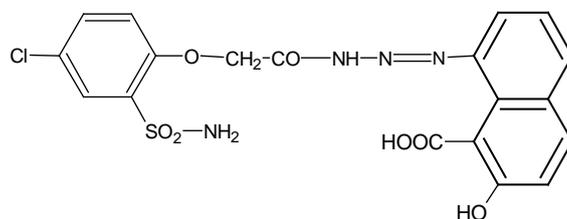

1-(3-{2-[4-(aminomethyl)phenoxy]ethyl}triaz-1-enyl)-2-naphthol **(1)**
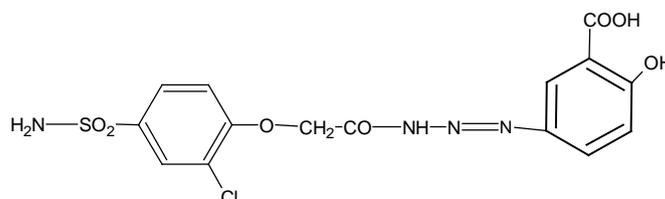Chemical formula: $C_{18}H_{16}N_4O_5S$
Molecular weight: 400
Melting point: 224-225^{0}C

8-(3-{2-[2-(aminomethyl)-4-chlorophenoxy]ethyl}triaz-1-enyl)
-2-hydroxy-1-naphthoic acid **(2)**
Chemical formula: $C_{19}H_{15}N_4O_7SCl$
Molecular weight: 478,5
Melting point: 214-218^{0}C

5-(3-{2-[4-(aminomethyl)-2-chlorophenoxy]ethyl}triaz-1-enyl)-2-hydroxybenzoic acid **(3)**
Chemical formula: $C_{15}H_{13}N_4O_7SCl$
Molecular weight: 428,5
Melting point: 190-193^{0}C

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Scheme 3 Samples under study (structure, molecular weight and melting points)

Thermal analysis

The thermogravimetric (TG) and differential thermal analysis (DTA) were performed by using a Perkin-Elmer Pyris Diamond TG/DTA thermobalance which records simultaneously the T, TG and DTA curves. The DTG curves were obtained by numerical differentiation of the TG curves. The working conditions were the following: sample mass 12 mg, heating rate 10 ^{0}C min^{-1}, temperature range 30-900 ^{0}C in nitrogen stream (800 ml min^{-1}).
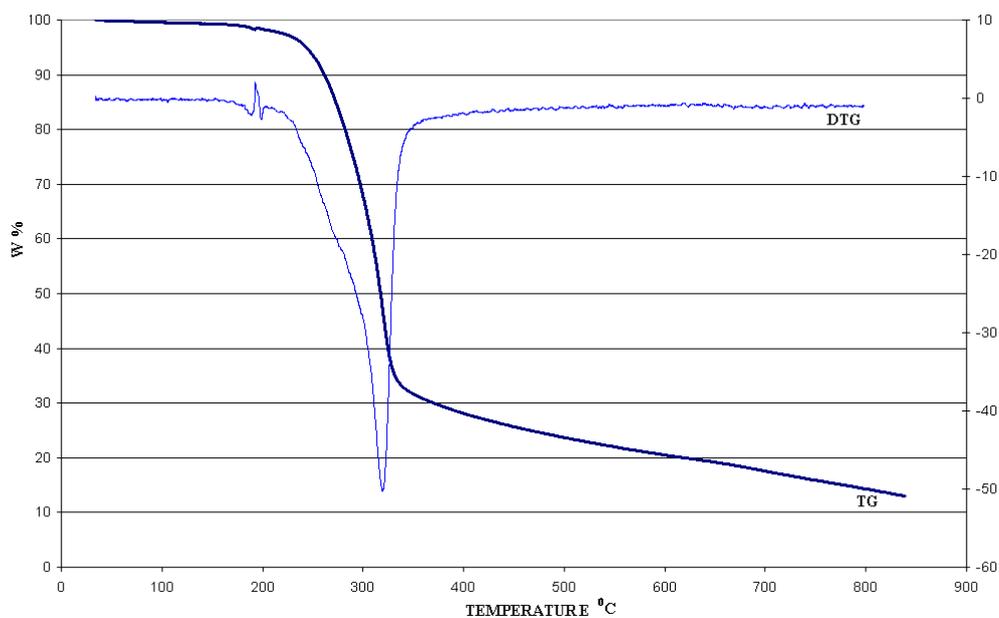
Results and Discussion

The The TG, DTG şi DTA curves of the diazoaminoderivatives in Scheme 3 are depicted in Fig. 1-3.
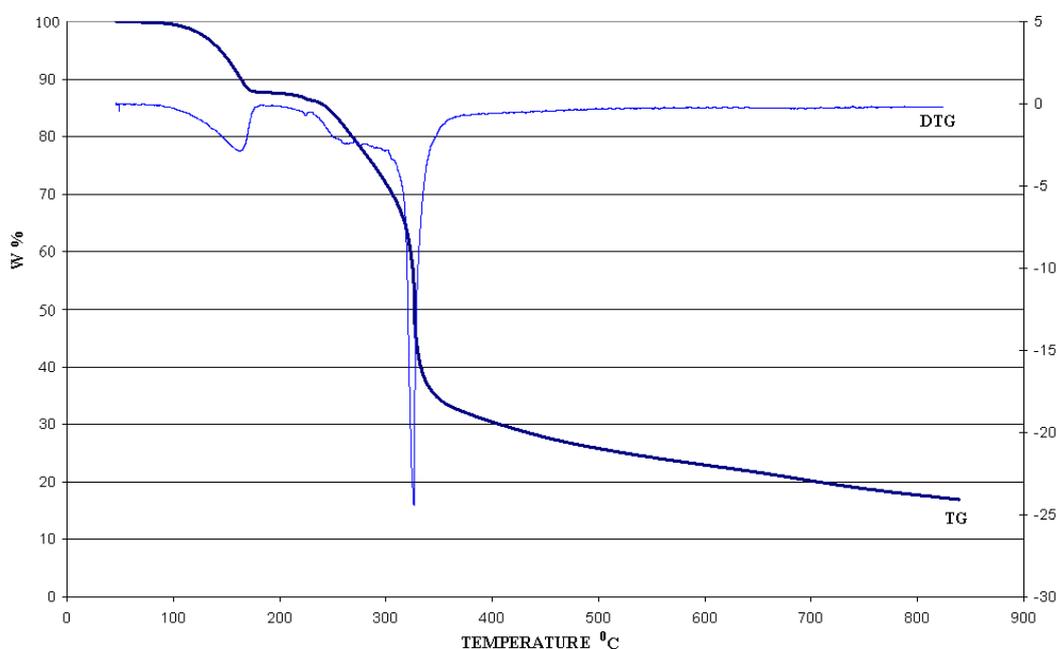
Figure 1. TG and DTG curves of the compound (**1**)
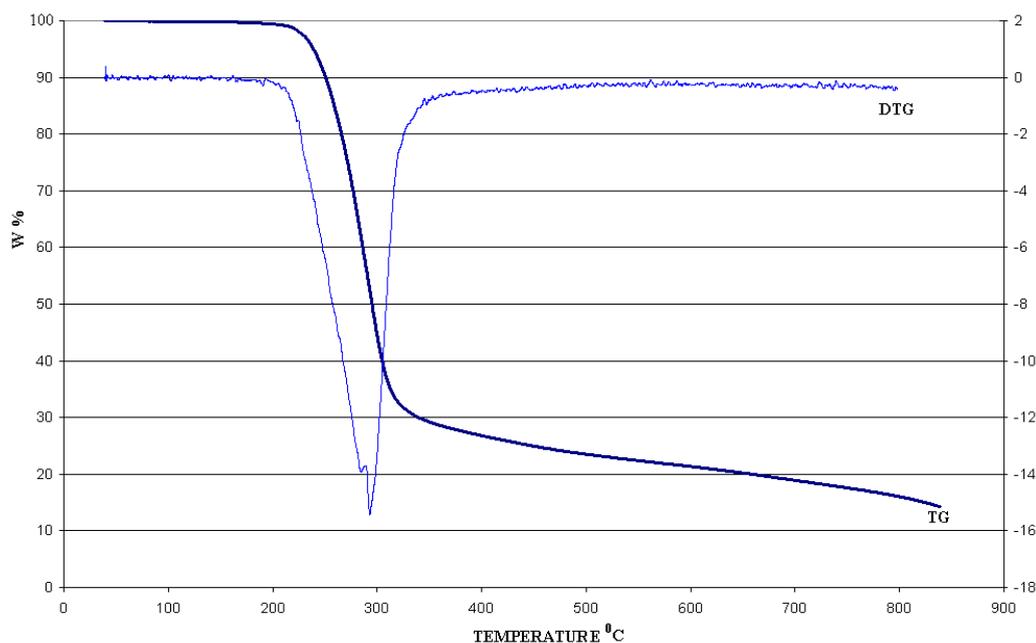
Figure 2. TG and DTG curves of the compound (**2**)

Figure 3. TG and DTG curves of the compound (**3**)

The examination of the TG and DTG curves affords the conclusion that the thermal degradation mechanism under nitrogen atmosphere, is specific and complex under the given working conditions, a similarity of the samples under study being noticed.

The diazoaminoderivatives under investigation were found to decompose into two stages, the first one being significant. The DTG curves show in this stage a clear inflexion point (compounds 1 and 3) while the sample 2 is seen to show two separated processes as revealed by the two curve maxima.

In table 1 the characteristic amounts resulting from TG – DTG are given:

$T_i \, ^0C$= initial degradation temperature;

$T_{inf} \, ^0C$= temperature corresponding to the inflexion point of the descending branch of the DTG curve

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$T_m {}^0C$= temperature corresponding to the maximum degradation rate;
$T_f {}^0C$= final degradation temperature;
$W\infty_{inf}$ %, $W\infty$ %= weight losses at the inflexion temperature, respectively, as well as resulting residue (%).

The fact can be noticed that the samples 2 and 3 do not retain the water. With the first sample, the weight losses in every stage were calculated after correcting the sample mass with the retained water.

Table 1. Characteristic amounts from TG-DTG curves.

Stage	Sample	1	2	3
Stage I	$T_i °C$	211.2	195.72	175.36
	$T_{inf} °C$	314.44	263.83	282.62
	$W_{\infty inf}$%	20.13	18.01	19.46
	$T_m °C$	330.24	282.75 290.29	316.68
	$T_f °C$	380.16	371.34	377
	W_∞%	34.32	69.96	52.14
Stage II	$T_i °C$	380.16	371.34	377
	$T_m °C$	900	900	900
	W_∞%	45.55	12.03	28.4
Residue	%	15.51	11.22	11.55
	Colour	brown	redish	white

As revealed by the data in Table 1, the first degradation stage, which is the significant one, develops within the $175,36^0C$- 380^0C temperature range while the second proceeds between 380^0C -900^0C.

The thermal stabilities of the samples expressed by T_i- initial temperature of thermal degradation under nitrogen atmosphere led to the following series: **1>2>3.**

A discussion on the stabilities of the three compounds under study by taking the electronic effects into account results in the following conclusions:

The main factor determining the stability of the three compounds is the electron- releasing effect (+E) of the ethereal oxygen. This effect is responsable for the electronic delocalization in the aromatic ring resulting in the double bond character given to the C-S bond which means that the higher the +E effect of the ethereal oxygen the higher the C-S bond order and the compound stability.

In case of the compound 1, the effect (+E) of the ethereal oxygen brings a contribution to the electronic delocalization in the aromatic ring and thus to the increase of the C-S bond strength to a IInd order bond, this compounds being more stable than the derivatives 2 and 3.

The compounds 2 and 3 contain a chlorine atom substituted in different positions towards the sulphonamidic group (S-C) in their aromatic ring. The chlorine atom showing a strong (-I) effect causes the stopping of the electronic delocalization in the aromatic ring at the carbon atom linked to the chlorine atom which results in the decrease of the C-S bond order and hence of the thermal stability of these compounds. The compounds 2 and 3 would show similar stabilities, the compound 2 being somehow less stable than 3 since the chlorine atom is located closer to the ethereal oxygen (ortho position).

The fact is thus made evident that the thermal stabilities of the three diazoaminoderivatives obey the same series found by means of the TG-DTG-DTA thermal analysis:

$$1 > 2 > 3.$$

The series of the thermal stabilities of the compounds under study is also confirmed by the values of the apparent activation energies estimated for the first chemical process corresponding to the NH_2-SO_2- group elimination by the S-C bond splitting. Two methods were applied on this purpose, the Chan-Balke differential method [12] and the Coats-Redfern integral method [13], the obtained results being presented in Table 2 .

Table 2 Kinetic parameters (n, E_a) of the initial reaction of thermal degradation

Sample	Chan-Balke method			Metoda Coats-Redfern		
	Reaction order (n)	Energy of activation Ea (Kj/mol)	Error R^2	Reaction order (n)	Energy of activation Ea (Kj/mol)	Error R^2
1.	1	122.96	0.991	1	120.0	0.985
2.	1	106.30	0.997	1	116.30	0.962
3.	1	188.59	0.960	1	190.60	0.997

The data in Table 2 reveal the following order of the activation energies:$E_{a1} > E_{a2} > E_{a3}.$ It can be noticed than the obtained values are close to the theoretical ones for this bond type.
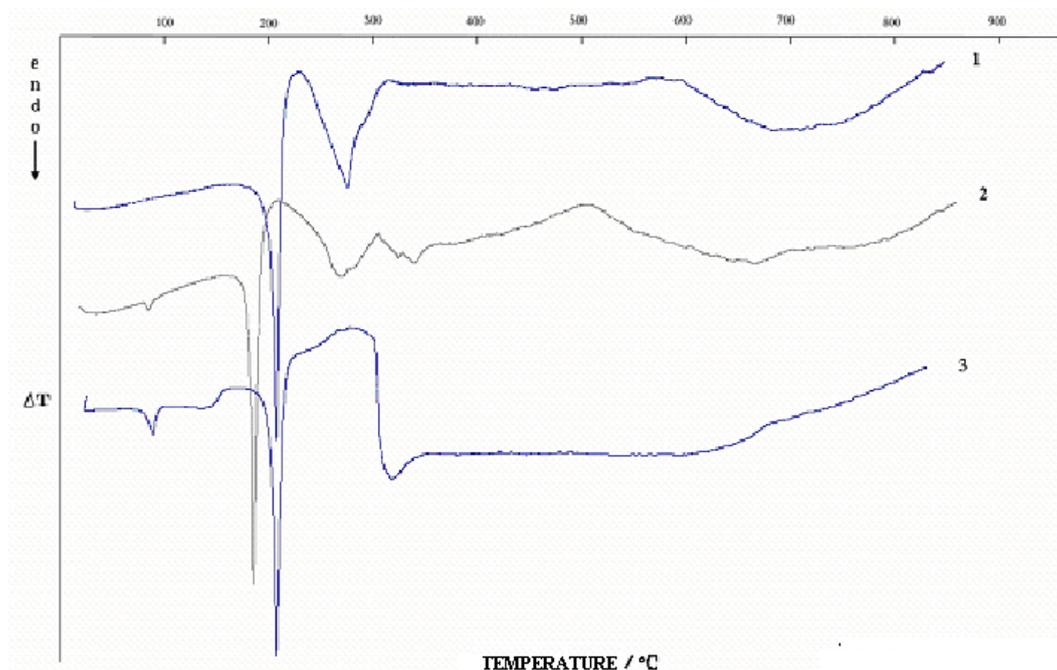
Figure 4. DTA curves of the samples (**1**), (**2**), (**3**).

The analysis of the DTA curves confirms the complex and specific mechanism resulting from the TG-DTG analysis , the same well-defined endothermic degradation stages being made evident. The diazoaminoderivatives show prior to the thermal degradation stages an endothermal peak within the 175^0C- 257^0C temperature range where the sample weights (TG-DTG) are constant corresponding to the melting peak.

The characteristic temperatures from DTA are given in Table 3.

Table 3 Characteristic temperatures from DTA

Sample	Melting			Stage I			Stage II		Thermal nature
	T_i ^{0}C	T_m ^{0}C	T_f ^{0}C	T_i ^{0}C	T_m ^{0}C	T_f ^{0}C	T_i ^{0}C	T_f ^{0}C	
1.	199.68	224.64	257.28	257.28	318.72	364.80	364.80	900	endo
2.	188.16	218.88	238.08	238.08	284.16	318.72	318.72	900	endo
3.	175	192	212	212	272 340	492	492	900	endo

The data in Table 3 indicate the same degradation temperature range as resulted from the TG-DTG, 174^{0}C -900^{0}C. The existence of two processes in the first degradation stage (compound 3) is made evident in DTA by the presence of two endothermic peaks, the former corresponding to the NH_2-SO_2- group elimination since the inflexion temperatures in TG-DTG correspond to the temperatures at the maximum of the first peak of the DTA curve.

For the second degradation process of the first stage the temperatures at the DTA peak maximum coincide with those in DTG at the maximum degradation rate which also supports the two chemical processes developing during the first stage.

The melting temperatures (Table 3) were estimated from the temperatures corresponding to the maximum of the DTA peak [14]

In table 4 the melting points of the samples estimated by both Boetius method and DTA are given which indicates the good agreement of the values thus obtained.

Table 4. Melting temperatures

Sample	T_m melting ^{0}C (DTA)	T melting ^{0}C Boetius Method
1.	224.64	224-225
2.	218.88	214-216
3.	192	190-193

The weight losses corresponding to the inflexion points in TG-DTG correlated with the structure and thermal stability of the azoderivatives under study afford a discussion on the degradation mechanism. Thus, the weight loss (%) corresponding to the first inflexion point (samples 1 and 3) and to the first process of the first stage, within the 175-330 ^{0}C temperature range, corresponds to the NH_2-SO_2- group elimination by the C-S group breakage. (Table 5).

Table 5 Experimental and theoretical weight losses for the (NH_2-SO_2-) group

Sample	Molecular weight	Temperature range T_i ^{0}C - T_{inf} ^{0}C	$W_{\infty inf}$ %, experimental (NH_2-SO_2-)	W_∞ %, theoretical (NH_2-SO_2-)
1.	400	211.2-314.44	20.13	20
2.	478.5	195.72-263.86	18.01	16.71
3.	428.5	175.36-282.52	19.46	18.66

The values of the kinetic parameters (n and Ea) estimated for this process (Table 3) confirm the development of a decomposition reaction since the reaction order, characteristic of such a reaction, is n=1 and the values of the energies of activation are close to those of the C-S bond energy.

It follows that the degradation mechanism involves an initial elimination of the NH_2-SO_2- group followed by chemical processes of specific degradation influenced subsequently by the nature of the substitutes in the molecule which results in a complex mechanism developing by successive reactions.

Conclusions

The analysis of the TG – DTG – DTA curves of the compounds under study is indicative of a complex and specific mechanisms of thermal degradation confirming the structure influence.

The elucidation of the behavior of the newly synthesized compounds would be useful for their characterizations if the possible applications as agrochemicals or as dyes are taken into account.

The thermal stabilities of the investigated compounds estimated by DTG and DTA methods obey the following series: **1 >2>3.**

The thermal stability is correlated to the chemical structure and the apparent energy of activation of the first chemical degradation process which affords the temperature range of using and storing these derivatives to be ascertained.

The melting points of the complexes estimated from DTA were in good agreement with those measured by the Boetius method.

The results of the thermal analysis correlated with the kinetic parameters for the first chemical process of the degradation afforded some appreciations to be made on the reaction mechanism when the first reaction of the complex mechanism developing by successive reactions was established

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