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TG-FTIR study on thermal degradation in air of some new diazoaminoderivatives (II)

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ABSTRACT

The TG-FTIR analysis of some new diazoaminoderivatives is aimed to follow the structure-thermal stability-degradation mechanism correlation. The TG–DTG–DTA curves are indicative of a complex and specific mechanism of thermal degradation in air of the diazoaminoderivatives under study which show a common characteristic regarding their degradation in air (30–900 °C) when two domains in function of temperature (time) can be noticed: an endothermic one, identical to the degradation under nitrogen atmosphere, and an exothermal one. The gaseous species resulting by degradation are also grouped in these domains.

The identification by means of the specific absorbances of every gaseous species and those obtained by TG-FTIR revealed that N_2, NH_3, $H_2C{=}NH$, SO_2, H_2O, CO_2, C_4H_8, C_3H_4 are eliminated within the first domain while SO_2, H_2O, CO_2 within the second. These results afforded the most probable thermal degradation mechanism to be advanced.

Since these compounds could show practical importance as initiators (generators of free radicals) and also as biologically active substances, their thermal stability and the degradation mechanism can give significant information on the temperature range proper for their practical application. Besides the compounds released by thermal degradation could give information about the potential environmental pollution.

1. Introduction

Going further with our studies in the field of thermal behavior of diazoaminoderivatives [1–4], in the present paper the structure-thermal stability-degradation mechanism correlation is reported for the following diazoaminoderivatives with potential biological activity by applying the FTIR technique: *4-(2-(3-(4-(dimethylamino)phenyl)triaz-2-en-1-yl)-2-oxoethoxy)-3-methylbenzenesulfonamide* (**a**), *5-chloro-2-(2-(3-(2,4-dihydroxyphenyl)triaz-2-en-1-yl)-2-oxoethoxy)benzenesulfonamide* (**b**), *5-amino-3-(3-(2-(4-chloro-2-sulfamoylphenoxy)acetyl)triaz-1-en-1-yl)-4-hydroxynaphthalene-2,7-disulfonic acid* (**c**).

In virtue of the practical importance of these compounds [4–8], the researches in recent years have been extended also over the group of sulfonamidated aryloxyalkylcarboxilic derivatives showing potential antitumoural, antioxidant, anti-inflammatory actions, being also useful in treatments of the ulcer, convulsions, diabetes [9–14]; apart from this, the potential herbicide action deserves mention [15–18].

The study on the thermal behavior of these compounds gives useful information on the temperature domain suitable for their stability, storage and practical applications. At the same time the degradation mechanism gives indications regarding the environmental impact of the degradation products when the initial degradation temperature is exceeded.

The analysis of the TG–DTG–DTA curves reveals that the thermal degradation in air (30–900 °C) shows two domains as a function of temperature (time): an endothermic one – which is identical to that for the degradation in nitrogen atmosphere [2]; and an exothermal one. These domains include also the release of the gaseous species resulting by degradation. The identification of the individual gaseous species by their characteristic absorbances [19] obtained by TG-FTIR analysis revealed the compounds NH_3, SO_2, $H_2C{=}NH$, CO_2, H_2O, HCl, C_4H_8, C_3H_4 to occur within the endothermic domain by weakly endothermic processes while within the strongly exothermal domain CO_2, SO_2, H_2O result by the oxidation of the molecular residues of the endothermic domain.

The obtained results were indicative of a good agreement of the melting points of the samples estimated by Boetius method and from the DTA curves. A good correlation was also noticed between the structure, thermal stability, appreciated from the initial degradation temperatures from TG and DTG, and the degra-

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dation mechanism advanced on the basis of the TG-FTIR analysis [4,20–29].

The thermal degradation mechanisms of the samples are complex and specific developing by successive-simultaneous reactions and depending on the structure and nature of the substitutes in the molecule. In the present paper degradation mechanism of every compound is advanced which was possible to be done by applying the TG-FTIR technique in order to follow the structure-thermal stability-degradation mechanism correlation.

2. Experimental

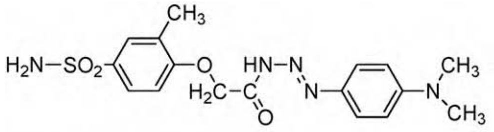
2.1. Materials

The chemical structure of the compounds under study, their formulae, IUPAC names, molecular weights and melting points measured by the Boetius method are given in Scheme 1.

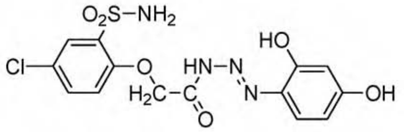
2.2. Methods

The TG-FTIR analyzer consists of a TG/DTA Diamond (PerkinElmer) thermo-balance and a FTIR spectrometer, Spectrum 100 (PerkinElmer), provided with a TG-FTIR (PerkinElmer) gas transfer accessory with a gas cell of 100 mm length and KBr windows, heated at 150 °C. The FTIR spectra were recorded within the 700–4000 cm^{-1} range at a resolution of 4 cm^{-1} and scanning rate of 200 $cm^{-1} s^{-1}$, a single spectrum being recorded every 15 s by means of the Spectrum Time Bose PerkinElmer program. A G7 gas analyzer (Dominic Hunter) supplies the dry air (pearl point: −50 °C) entering the TG/DTA analyzer at a flow rate of 100 mL min^{-1} as well as the nitrogen for purging the analysis room of the FTIR spectrophotometer. The analysis was run with 10 mg sample placed into a platinum crucible, at a heating rate of 10 K min^{-1} within the 30–900 °C temperature range. The DTG curves are obtained by numerical derivation of the TG curves.

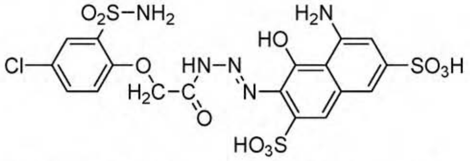
The qualitative identification of the gaseous species resulting by thermal degradation was made with the IR standard spectra [19].



4-(2-(3-(4-(dimethylamino)phenyl)triaz-2-en-1-yl)-2-oxoethoxy)-3-methylbenzenesulfonamide **(a)**
Chemical formula: $C_{17}H_{21}N_5O_4S$
Molecular weight: 391.44
Melting point: 145-149°C with decomp.



5-chloro-2-(2-(3-(2,4-dihydroxyphenyl)triaz-2-en-1-yl)-2-oxoethoxy)benzenesulfonamide **(b)**
Chemical formula: $C_{14}H_{13}ClN_4O_6S$
Molecular weight: 400.79
Melting point: 219-224°C with decomp.



5-amino-3-(3-(2-(4-chloro-2-sulfamoylphenoxy)acetyl)triaz-1-en-1-yl)-4-hydroxynaphthalene-2,7-disulfonic acid **(c)**
Chemical formula: $C_{18}H_{16}ClN_5O_{11}S_3$
Molecular weight: 609.99
Melting point: 221-223°C with decomp.

Scheme 1. Samples under study (structure, molecular weight and melting points).

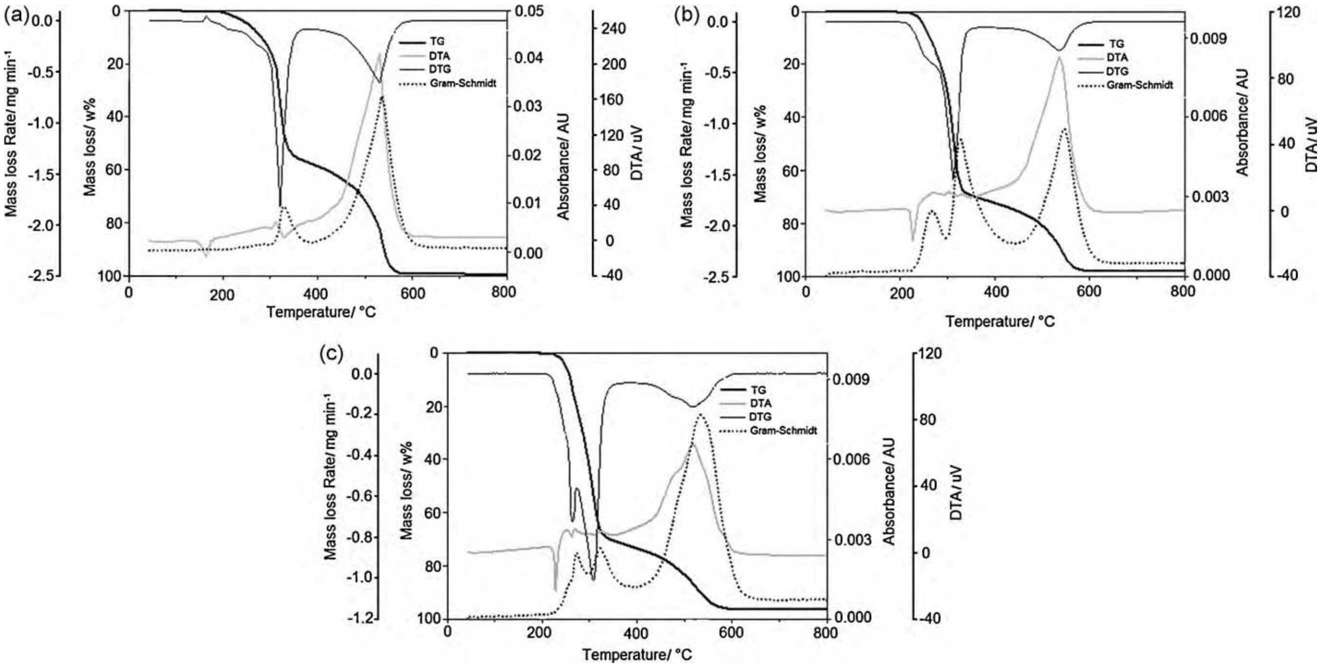


Fig. 1. (a) TG, DTG, DTA and Gram–Schmidt curves of the compound (**a**). (b) TG, DTG, DTA and Gram–Schmidt curves of the compound (**b**). (c) TG, DTG, DTA and Gram–Schmidt curves of the compound (**c**).

Table 1
Characteristic amounts from TG–DTG–DTA analysis.

Thermal method	Temperature range	Stage	Characteristic temperatures	Sample		
				a	b	c
TG–DTG	100–370 °C	I	T_i, °C	175.00	231.25	227.54
			T_{inf}, °C	243.75	243.75	240.62
			W_∞, %	6.00	6.84	4.56
			T_m, °C	318.75	315.62	259.37
			T_f, °C	362.50	362.50	278.12
			W_∞, %	20.00	26.92	30.25
		II	T_i, °C	–	–	278.12
			T_m, °C	–	–	312.50
			T_f, °C	–	–	362.50
			W_∞, %	40.00	47.00	49.00
	400–600 °C	III	T_i, °C	362.50	362.50	362.50
			T_{inf}, °C	–	–	475.00
			T_m, °C	534.37	540.60	518.75
			T_f, °C	600.00	600.00	600.00
			W_∞, %	40.00	26.08	21.75
	Residue %			0.00	3.14	4.56
DTA	100–370 °C (endothermic domain)		$T_{melting}$, °C	143.05	219.06	220.19
			T_{mI}, °C	320.00	317.00	262.50
			T_{mII}, °C	–	–	313.00
	370–600 °C (exothermal domain)		T_i, °C	362.50	362.50	362.50
			T_{inf}, °C	–	–	475.30
			T_m, °C	534.50	540.60	518.75
			T_f, °C	600.00	600.00	600.00

T_i = initial thermal degradation temperature; T_{inf} = inflexion point temperature. T_m = temperature at the maximum degradation rate; T_f = final thermal degradation temperature. W_∞ (%) = weight loss (%).

3. Results and discussion

The TG, DTG and DTA curves obtained with the compounds under study in air atmosphere are depicted in Fig. 1a–c.

The TG, DTG and DTA curves are indicative of a complex and specific thermal degradation mechanism for every sample under the recording conditions. The samples show two ranges concerning the thermal nature of the degradation processes: a slightly endothermic domain between 100 and 370 °C and the other strongly exothermal between 370 and 600 °C. This finding was also noticed with other four diazoaminoderivatives previously studied by the same TG-FTIR technique. The fact also deserves mention that the diazoaminoderivatives studied in our previous and present papers show a degradation mechanism within the endothermic domain similar to that under nitrogen atmosphere [2].

Within the endothermic domain the compounds **a** and **b** are degraded into one stage where the DTG curves show clear inflexions being non-symmetrical, while the corresponding DTA curves show slightly endothermic peaks which would suggest successive reactions developing by the break of certain molecular bonds. Within the same endothermic domain the compound **c** is degraded into two stages unclearly separated, the DTG curve showing inflexion points while on the DTA curve two weakly endothermic peaks are accordingly to be found, which would suggest a degradation mechanism more complex than with the samples **a** and **b**.

Within the exothermal domain the DTG and DTA curves of every sample are unsymmetrical. The inflexion points are more significant with the sample **c**, which is indicative of a stepwise oxidative degradation of the molecular residues remaining after the first degradation stage.

With every sample the endothermic degradation domain occurs subsequently to a strongly endothermic process where the sample weight remains constant corresponding to the melting peak of the sample.

In Table 1 the characteristic temperatures from TG–DTG–DTA curves and the weight losses in every stage of the endothermic and exothermal domains are given.

The data in Table 1 are indicative of a good agreement between the melting points estimated from DTA [30] analysis and those resulting by the Boetius method (Scheme 1).

The initial thermal degradation temperatures from TG–DTG (Table 1) indicate the following thermal stability series:

b > **c** > **a**

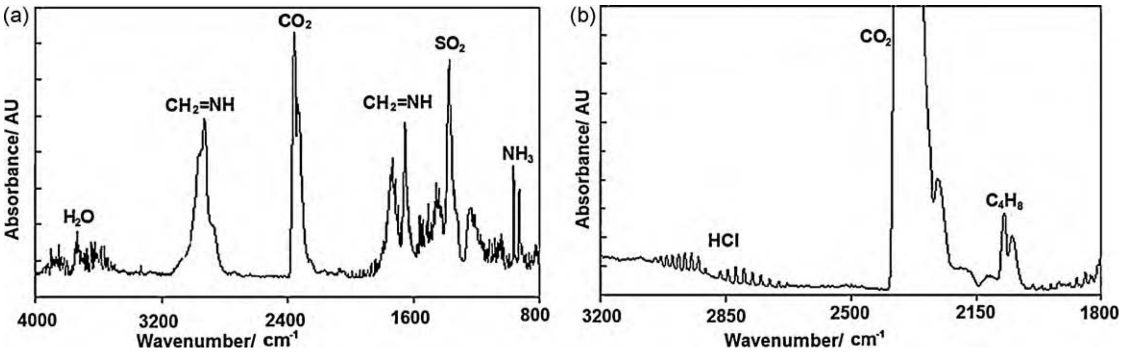


Fig. 2. (a) FTIR spectrum for gaseous products evolving from sample **b** (25.6 min). (b) FTIR spectrum for gaseous products evolving from sample **b** (40.1 min).

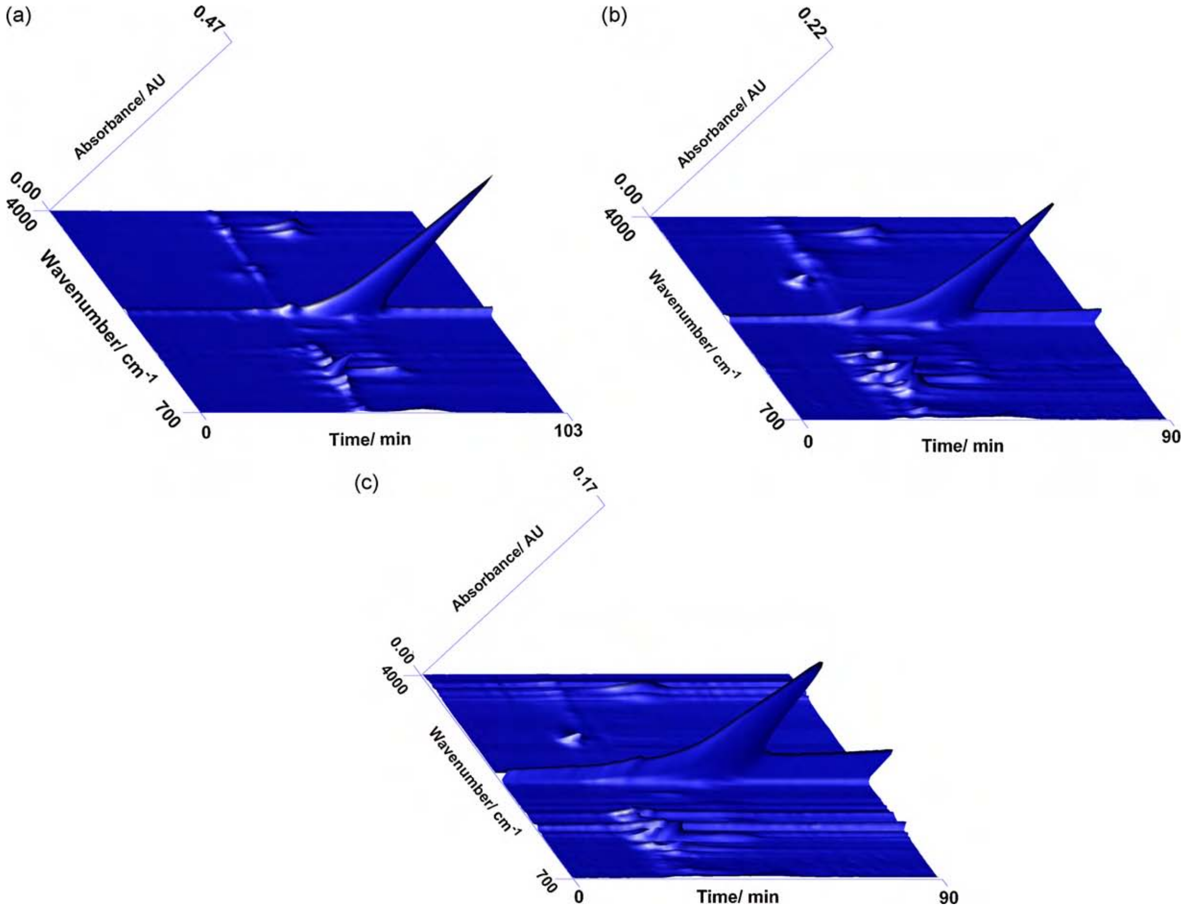


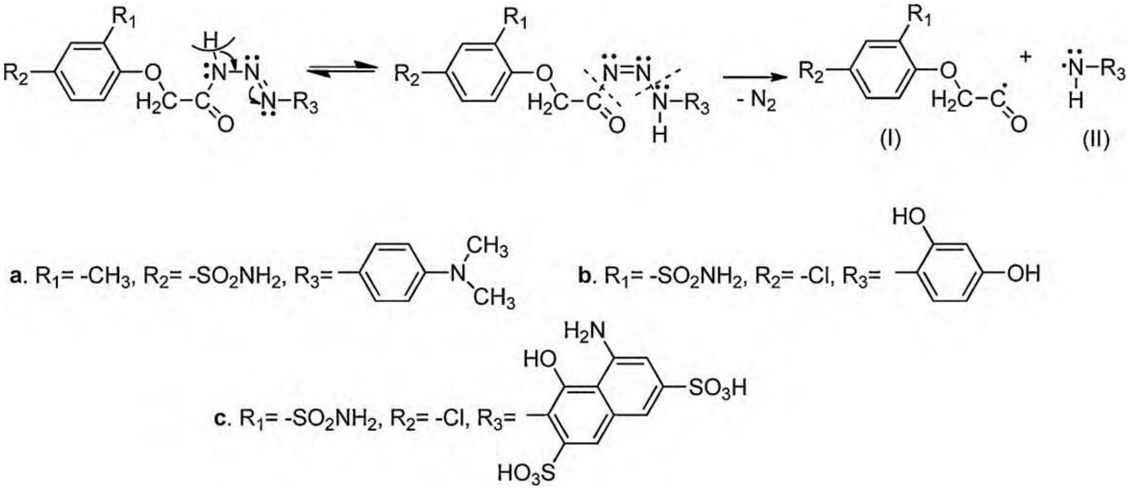
Fig. 3. (a) 3DFTIR spectra obtained for the thermal degradation of the sample (**a**). (b) 3DFTIR spectra obtained for the thermal degradation of the sample (**b**). (c) 3DFTIR spectra obtained for the thermal degradation of the sample (**c**).

The same order of the melting points was noticed. The temperatures corresponding to the inflexion in the first degradation stage within the 100–370 °C range are the same with all the samples under study which would suggest the same chemical process to develop (Table 1).

The temperatures corresponding to the maximum rate are the same for the samples **a**, and **b** being coincidental with those resulting from DTA analysis. For sample **c**, an additional process occurs in the first stage of degradation. Since the temperatures T_m and T_f for sample **c** are the same, the process from the second stage is similar to process from the case of the samples **a**, and **b**.

In the exothermal domain, the temperatures T_m from DTG and DTA are the same with processes between 518.75 and 540.6.

The data in Table 1 reveal that the weight losses (%) at the inflexion point of the DTG curves in the stage I within the endothermic domain between 30 and 370 °C is coincidental with the weight (%) corresponding to the nitrogen elimination from the molecules of the samples.



Scheme 2.

Table 2
Theoretical (W_t, %) and experimental (W_{exp},%) weight losses of the samples by nitrogen elimination at T_{inf}.

Sample	$W_{experimental}$	$W_{theoretical}$
a	6.00	7.16
b	6.84	6.99
c	4.56	4.59

In Table 2 the theoretical weight losses due to the nitrogen elimination (W_t, %) and those corresponding to the inflexion temperatures (W_{exp}, %) are given.

The good agreement noticed with these amounts affords the conclusion that the thermal degradation of the samples begins with the nitrogen elimination as expected.

By the FTIR analysis of the gases evolved by the thermal degradation in air using standard IR spectra [19] the following gaseous species were identified: SO_2, NH_3, CO_2, $CH_2{=}NH$, C_3H_4, C_4H_8 (sample **a**), SO_2, NH_3, CO_2, HCl, C_4H_8, H_2O (sample **b**) and SO_2, NH_3, CO_2, HCl, C_4H_8, H_2O (sample **c**).

The nitrogen eliminated at the beginning of the thermal degradation within the endothermic domain made evident by TG–DTG analysis could not be identified by FTIR analysis since the degradation in air containing about 78% N_2 does not afford this identification.

For exemplification the FTIR spectra of the gaseous species resulting by the thermal degradation in air of the sample **b**, at time 25.6, and 40.1 min are depicted in Fig. 2a and b, respectively.

The Gram–Schmidt curves drawn in Fig. 1a–c reveal the elimination of the gaseous species to proceed over two temperature domains corresponding to the endothermic and exothermal domains from TG–DTG–DTA analysis.

These findings can also be noticed in Fig. 3a–c illustrating the 3DFTIR spectra of the gaseous species evolved by the thermal degradation in air of the samples **a**–**c**.

The dependence of IR absorbances with temperature for the identified gaseous species are depicted in Fig. 4a and b.

The weight losses over the endothermic and exothermal domains (W_{exp}, %) and of the eliminated gaseous components (W_t, %) afforded the data in Table 3.

A good agreement is noticed affording the advancement of the most probable thermal degradation mechanism in air of the samples under study.

The thermal stability order of the compounds under study along with the considerations on the thermal degradation in air of the samples **a**–**c**, on the basis of the FTIR analysis, are also supported by their structure and by the general thermal behavior of the azocompounds. As shown in our previous papers the azocompounds are thermally unstable being easily decomposed with nitrogen elimination; the N_2 molecule is a fugacious group and this is why some of the azoderivatives are used as radical initiators [31]. With these new diazoaminoderivatives we are indebted to admit that the nitrogen molecule is also responsible for the most possible fragmentation as noticed by the TG–DTG analysis (Table 2). Thus, if the diazoaminoderivatives under study (Scheme 1) are supposed to decompose starting with nitrogen elimination by an endothermic process two radical fragments, I and II, occur (Scheme 2).

The samples **b** and **c** are noticed to give the same radical fragment, (I), with substitutes in the same positions. In this case the stabilities of the compounds **b** and **c** would be influenced only by the substitutes R_1 and R_2 that are the same and placed at the same posi-

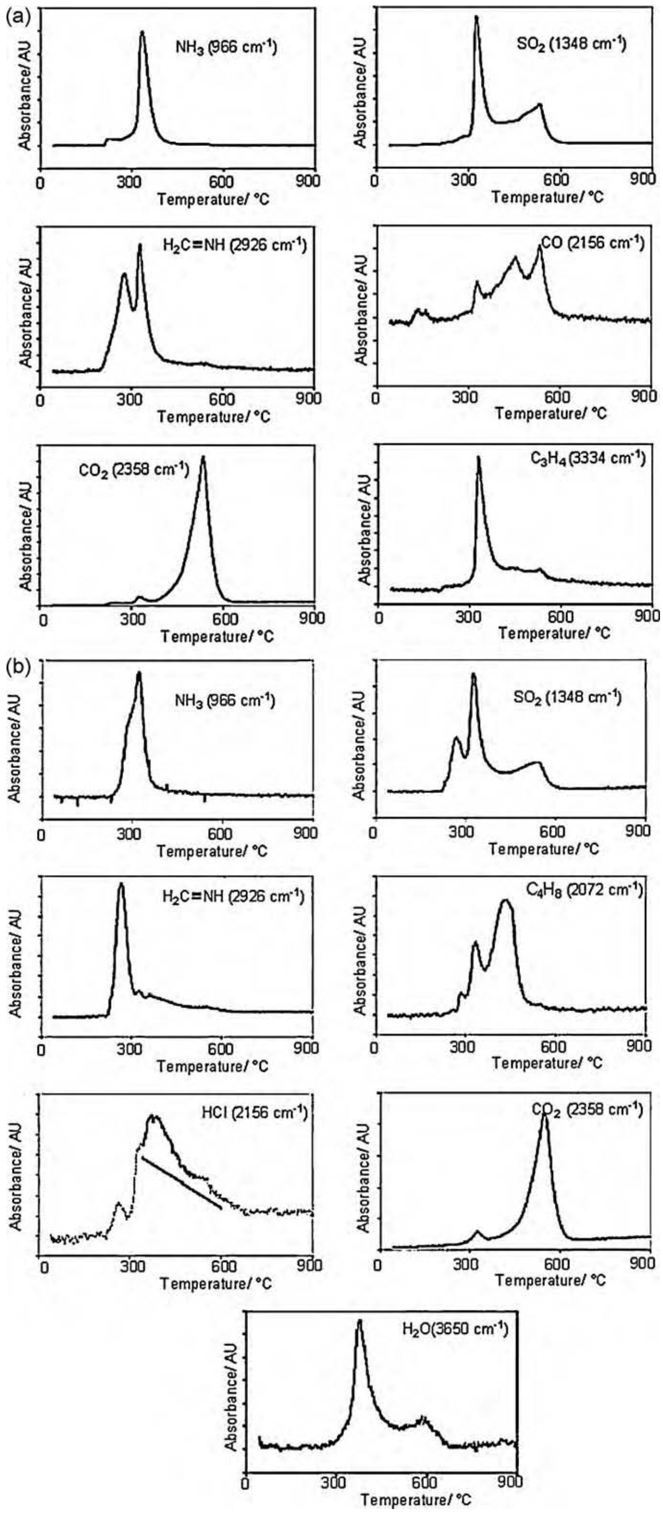
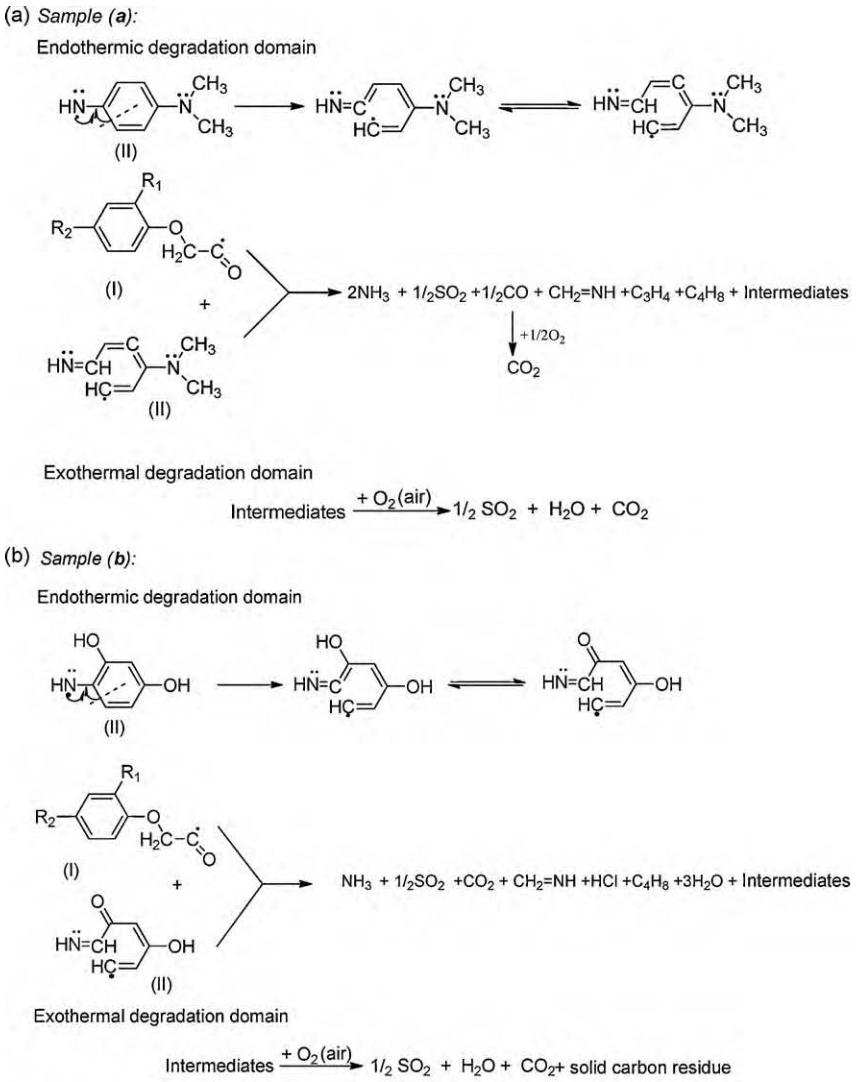


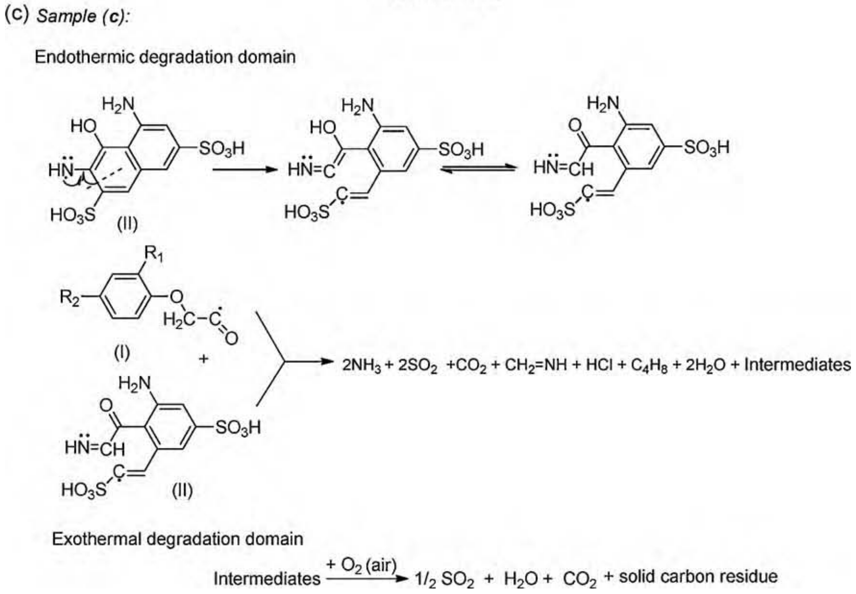
Fig. 4. (a) IR absorbance versus temperature curves of identified evolved gaseous species from sample **a** in air. (b) IR absorbance versus temperature curves of identified evolved gaseous species from samples **b** and **c** in air.

Table 3
Weight losses in the endothermic and exothermal domains (W_{exp},%, from TG) and weight of the evolved gaseous components (W_t,%, obtained by the summing of the weights of the evolved gaseous compounds in the endothermic domain, and by the subtraction of the previous value and of residue value from 100%, in the exothermal domain).

Sample	Endothermic domain		Exothermal domain		Residue, %
	W_{exp}, %	W_t, %	W_{exp}, %	W_t, % + residue, %	
a	56.01	56.01	43.99	43.99	0.00
b	70.48	70.53	26.10	29.47	3.42
c	62.07	61.93	33.37	38.07	4.56



Scheme 3.b.



Scheme 3.

tion, the thermal stabilities of the samples should be the same and so should be the initial degradation temperatures but since $T_{ib} > T_{ic}$ it follows that the substitutes in the radical fragment II influence the strength of the –C–N═N– bond.

In compounds **b** and **c** the –OH group in *ortho* position, with respect to the –C–N═N– group, is favorable to the formation of hydrogen bonds between the nitrogen atoms and hydrogen in the phenol –OH group (Scheme 1). Due to the hydrogen bond, the nitrogen elimination becomes more difficult and consequently the compounds **b** and **c** containing the same hydrogen bond show higher thermal stabilities than the compound **a**. Apart from that, as already mentioned in a previous paper [4], the presence of the electron-withdrawing substitutes in the aromatic ring containing also the diazo (–N═N–) group results in an increased thermal stability of the diazoaminoderivatives by strengthening the –C–N═N– bond and hindering thus the nitrogen elimination. In contrast to that, the electron-releasing substitutes could be supposed to promote the nitrogen elimination since the –C–N═N– bond is not any more strengthened.

The dimethylamino group, $-N(CH_3)_2$, in the structure of the compound **a** shows a strong electron-releasing effect and thus the compound **a** would eliminate nitrogen more easily being less stable than **b** and **c**.

The compound **b** is more stable than **c** even the last contains the $-SO_3H$ electron-withdrawing group. This group in the *ortho* position with respect to –C–N═N– and the $-NH_2$ group show a steric interaction and thus although the SO_3H group should strength the –C–N═N– bond this one is easier split.

On the basis of these structure considerations involving the substitute influences on the –C–N═N– bond the resulting thermal stability order is identical to that given by the TG–DTG analysis:

b > **c** > **a**

Based on the TG-FTIR analysis of the structures under study as well on the elimination order of the gaseous species (Fig. 4a and b) the most probable degradation mechanism was advanced (Scheme 3) for the thermal degradation in air under the TG–DTG analysis conditions.

4. Conclusion

The study on the structure-thermal stability-degradation mechanism correlation of three new diazoaminoderivatives affords the following conclusions:

- The TG–DTG–DTA analysis of the compounds under study is indicative of a complex and specific thermal degradation mechanism in air where two domains were found: an endothermic one, identical to the case of the degradation under nitrogen atmosphere, and the other exothermal as a function of temperature.
- The characteristic temperatures resulting from the TG–DTG–DTA analysis are indicative of a good agreement between the melting points (DTA) and those measured by the Boetius method; the initial degradation temperatures afford the following order of thermal stability sustained also by the chemical structure of the compounds under consideration:

  b > **c** > **a**
- The degradation domains found by TG–DTG–DTA analysis of the samples are in agreement with the grouping of the spectra of the eliminated gaseous species.
- Based on the identification of the gaseous species eliminated by thermal degradation over the endothermic (NH_3, SO_2, $H_2C{=}NH$, CO_2, H_2O, HCl, C_4H_8, C_3H_4) and exothermal (SO_2, CO_2, H_2O) domains as well as on the TG–DTG–DTA analysis the most probable thermal degradation mechanism was advanced for the diazoaminoderivatives under study.
- The structure correlation with thermal stability and degradation mechanism brings valuable information on both the temperature range of using and storing these compounds and the possible environmental impact of the gaseous degradation products evolved when the initial degradation temperature is exceeded.

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