

Comparative study on thermal degradation of some new diazoaminoderivatives under air and nitrogen atmospheres

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Abstract The article is devoted to a comparative study on the thermal degradation of some new diazoaminoderivatives under both air and nitrogen atmosphere by TG-FTIR analysis. The TG-DTG-DTA curves show the thermal degradation in air to present two temperature domains: an endothermic one identical to the case of the degradation under nitrogen and an exothermic one which is not to be found under nitrogen atmosphere. The identification of the gaseous species released by degradation in air within the endothermic domain made evident the presence of the same components of the degradation in nitrogen atmosphere. In the exothermic domain of the sample degradation in air, the CO₂, H₂O, SO₂ species result by the burning of the molecular residues of the first domain. The obtained results afforded a degradation mechanism to be advanced that coincide for the endothermic domain with that of degradation under nitrogen atmosphere. Due to the importance of these compounds as possible reaction initiators and also as potentially bioactive substances (herbicides, acaricides, fungicides), the study on their thermal degradation could give useful information on the environmental impact of the degradation products resulting by the thermal processing of the plants which could possible retain these compounds, when the initial degradation temperature is exceeded.

Keywords Diazoaminoderivatives · Degradation mechanism · TG-FTIR · Thermal degradation · Thermal stability

Introduction

In this article, our previous studies [1–4] on the thermal behavior of potentially active compounds are extended by applying the TG-FTIR technique over some new diazoamino-derivatives able to be used either as reaction initiators [5] or as potentially bioactive compounds (herbicides, acaricides, fungicides) [6–10].

The comparative study of the structure-thermal stability-degradation mechanism correlation made under both air and nitrogen atmosphere with three new diazoaminoderivatives, 3-chloro-4-((1-(3-(4-(dimethylamino)phenyl)triaz-2-en-1-yl)-1-oxopropan-2-yl)oxy)benzenesulfonamide (**a**), 3-chloro-4-((1-(3-(2-hydroxynaphthalen-1-yl)triaz-2-en-1-yl)-1-oxopropan-2-yl)oxy)benzenesulfonamide (**b**), 5-(3-(2-(2-chloro-4-sulfamoylphenoxy)propanoyl)triaz-1-en-1-yl)-6-hydroxynaphthalene-2-sulfonic acid (**c**), gives useful information on the temperature range where these compounds are stable and can be stored and used, while the elucidation of the degradation mechanism is useful for predicting the eventual environmental impact of the degradation products resulting by certain processing exceeding the initial degradation temperature.

The analysis of the TG-DTG-DTA curves [11–13] reveals the thermal degradation in air (30–900 °C) to be specific and complex showing two domains as a function of temperature (time): an endothermic one which is identical to that for the degradation in nitrogen atmosphere and an exothermic one that cannot be found if the degradation take

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place under nitrogen, these domains include also the gaseous species resulting by degradation.

The identification of the individual gaseous species released within the endothermic domain under both air and nitrogen atmosphere revealed the same compounds to result with every sample but different from one sample to another. Within the exothermic domain of the degradation in air the burning of the molecule residues of the first domain gives CO_2 , H_2O , and SO_2 . For all samples, the weight losses noticed with the degradation in air in the endothermic domain correspond to those noticed under nitrogen atmosphere. By taking this result into account along with the finding that the characteristic temperatures from TG–DTG–DTA are the same for the air and nitrogen degradations within the endothermic domain, it follows that the degradation mechanisms are also the same within the 30–350 °C temperature range.

The obtained results afforded the most probable degradation mechanism in air and in nitrogen to be advanced as a complex one proceeding as successive-simultaneous reactions.

A good structure–thermal stability–degradation mechanism correlation was found by applying the very efficient TG-FTIR technique [4, 14, 15].

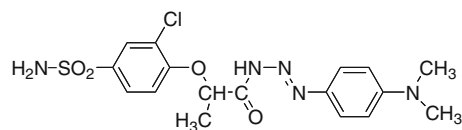
Experimental

Materials

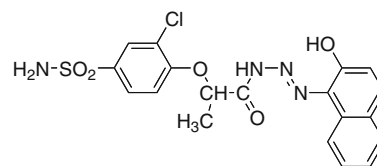
The chemical structure of the compounds under study, their formulae, IUPAC names, molecular weights, and melting points measured by the Boetius method are given in Scheme 1.

Methods

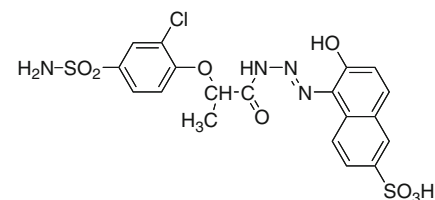
The TG-FTIR analyzer consists of a TG/DTA Diamond (Perkin Elmer) thermo-balance and a FTIR spectrometer, Spectrum 100 (Perkin Elmer), provided with a TG-FTIR (Perkin Elmer) gas transfer accessory and a gas cell of 100 mm length and KBr windows, heated at 150 °C. The FTIR spectra were recorded within the 700–4000 cm^{-1} range at a resolution of 4 cm^{-1} and scanning rate of 200 $\text{cm}^{-1}\text{s}^{-1}$, a single spectrum being recorded every 15 s. by means of the Spectrum Time Base Perkin Elmer program. The Gram–Schmidt diagrams represent the variation of all IR spectrum with the temperature for all gaseous species that are eliminated upon thermal degradation of sample, and are obtained by the summing (and the grouping) of the gaseous species as function of temperature (time). A G7 gas analyzer (Dominic Hunter) supplies the dry air (pearl point: –50 °C) entering the TG/DTA analyzer



3-Chloro-4-((1-(3-(4-(dimethylamino)phenyl)triaz-2-en-1-yl)-1-oxopropan-2-yl)oxy)benzenesulfonamide (a)
Chemical formula: $\text{C}_{17}\text{H}_{20}\text{N}_5\text{O}_4\text{SCl}$
Molecular weight: 425,5
Melting point: 138–140 °C



3-Chloro-4-((1-(3-(2-hydroxynaphthalen-1-yl)triaz-2-en-1-yl)-1-oxopropan-2-yl)oxy)benzenesulfonamide (b)
Chemical formula: $\text{C}_{19}\text{H}_{17}\text{N}_4\text{O}_5\text{SCl}$
Molecular weight: 448,5
Melting point: 105 °C



5-(3-(2-(2-Chloro-4-sulfamoylphenoxy)propanoyl)triaz-1-en-1-yl)-6-hydroxynaphthalene-2-sulfonic acid (c)
Chemical formula: $\text{C}_{19}\text{H}_{17}\text{N}_4\text{O}_8\text{S}_2\text{Cl}$
Molecular weight: 528,5
Melting point: 135–137 °C

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

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.

Results and discussion

The TG, DTG, and DTA curves obtained with the compounds under study in air and nitrogen atmosphere, respectively, are depicted in Figs. 1a–c and 2a–c.

The TG, DTG, and DTA curves are indicative of a complex and specific thermal degradation mechanism for every sample. The samples show two ranges regarding the thermal nature of the degradation processes: a slightly

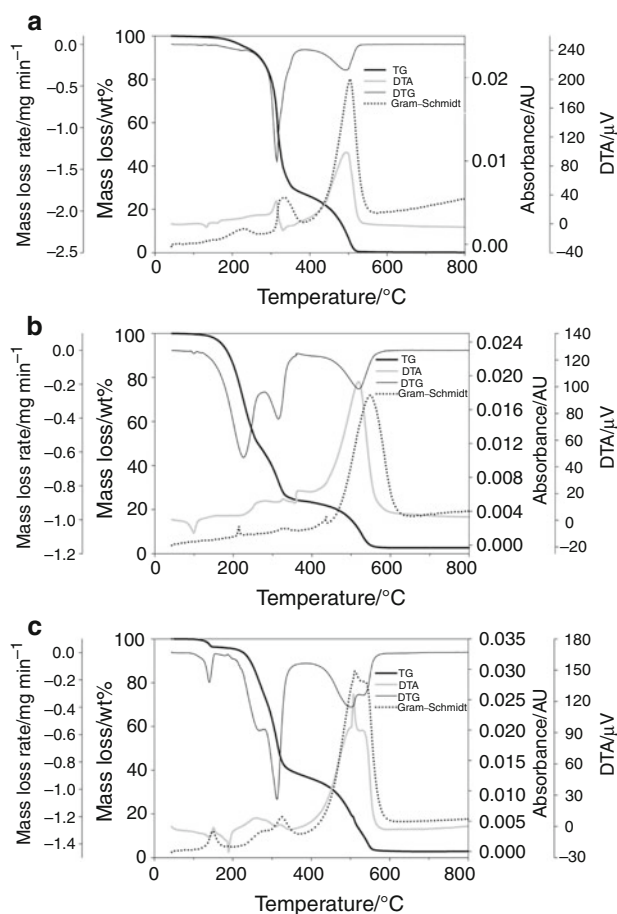


Fig. 1 **a** TG, DTG, DTA, and Gram–Schmidt curves of the compound **a** in air. **b** TG, DTG, DTA, and Gram–Schmidt curves of the compound **b** in air. **c** TG, DTG, DTA, and Gram–Schmidt curves of the compound **c** in air

endothermic domain between 30–350 °C and the other strongly exothermic between 350–600 °C. The degradation mechanism in nitrogen atmosphere (Fig. 2a–c) is noticed to be similar to that in air within the endothermic domain, the thermograms being identical over the 30–350 °C range with every sample.

In air and in nitrogen, the compound **a** is degraded into one stage within the endothermic domain, while two stages not clearly separated are noticed for the compounds **b** and **c** as expected due to their similar structures (Scheme 1).

In the first stage, the compounds under study show a clear inflexion point at 239.02 °C (sample **a**), 175.69 °C (sample **b**), 210.79 °C (sample **c**), respectively, and a slightly endothermic process is evident in DTA suggesting the splitting of similar bonds.

In the exothermic domain of the degradation in air the DTG and DTA curves are not symmetrical. The inflexion points are more marked with the sample **c** which would be indicative for this temperature range (350–600 °C) of oxidations of the molecular residues resulting in the first

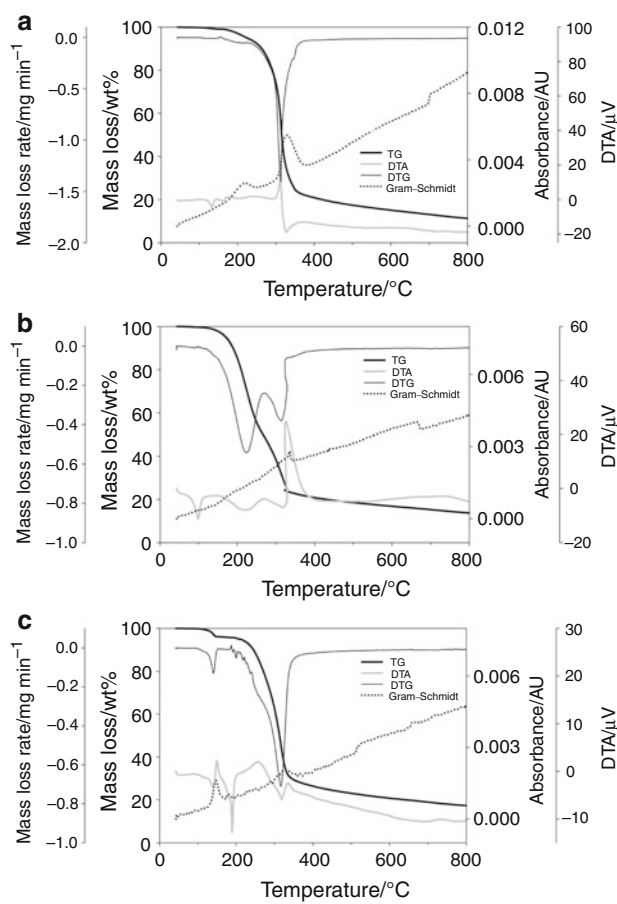


Fig. 2 **a** TG, DTG, DTA, and Gram–Schmidt curves of the compound **a** in nitrogen atmosphere. **b** TG, DTG, DTA, and Gram–Schmidt curves of the compound **b** in nitrogen atmosphere. **c** TG, DTG, DTA, and Gram–Schmidt curves of the compound **c** in nitrogen atmosphere

domain, a process which develops gradually by strongly exothermic reactions.

The endothermic degradation domain in air and in nitrogen is preceded by a marked endothermic process when the sample mass remains constant, which correspond to the melting peak of the samples.

In Table 1, the characteristic amounts from TG–DTG–DTA for the degradation in air and in nitrogen are given.

The data in Table 1 are indicative of a good agreement between the melting points estimated from DTA [16] and those resulting by the Boetius method (Scheme 1).

The initial thermal degradation temperatures from TG–DTG, both in air and in nitrogen, are the same (Table 1) and indicate the following thermal stability series:

$$\mathbf{c} > \mathbf{b} > \mathbf{a}$$

by taking also the fact into account that

$$T_{i(c)} > T_{i(b)} > T_{i(a)}$$

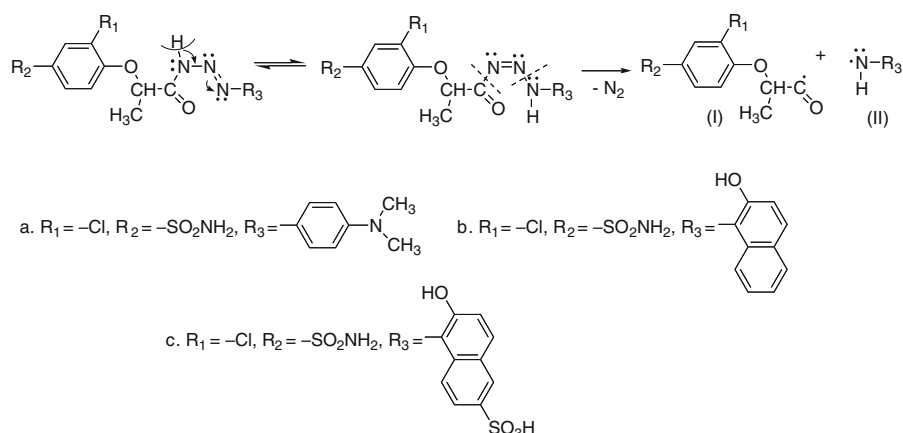
The thermal stability order of the compounds under study is supported by their structure [17]. Thus, in case of

Table 1 Characteristic amounts from TG–DTG–DTA analysis

Thermal method	Temperature range	Stage	Characteristic temperatures		Sample		
					a	b	c
TG–DTG	30–350 °C	I	$T_i/^\circ\text{C}$	Air	107.00	112.73	124.09
				N ₂	109.63	111.19	121.58
			$T_{inf}/^\circ\text{C}$	Air	239.02	175.69	210.79
				N ₂	241.35	170.0	209.23
			$W_{\infty inf}/\%$	Air	5.62	5.87	4.93
				N ₂	6.54	5.00	5.03
		$T_m/^\circ\text{C}$	Air	315.30	229.24	271.94	
			N ₂	312.91	227.46	273.98	
		$T_f/^\circ\text{C}$	Air	374.05	281.62	284.02	
			N ₂	374.00	271.88	289.11	
		$W_{\infty}/\%$	Air	77.62	54.96	27.51	
			N ₂	77.83	51.63	24.84	
	II		$T_i/^\circ\text{C}$	Air	–	281.62	284.02
				N ₂	–	271.88	289.11
			$T_m/^\circ\text{C}$	Air	–	317.18	314.00
				N ₂	–	316.48	317.43
			$T_f/^\circ\text{C}$	Air	–	364.36	390.82
				N ₂	–	364.29	393.98
	$W_{\infty}/\%$	Air	–	20.88	35.75		
		N ₂	–	26.31	43.45		
	350–600 °C	III	$T_i/^\circ\text{C}$	Air	374.05	364.36	390.82
				N ₂	–	–	–
			$T_m/^\circ\text{C}$	Air	497.67	512.78	508.39
				N ₂	–	–	–
$T_f/^\circ\text{C}$			Air	537.03	590.15	587.71	
			N ₂	–	–	–	
$W_{\infty}/\%$		Air	22.38	21.46	32.80		
		N ₂	–	–	–		
$W_{\infty t}/\%$		Air	100.00	97.30	96.06		
		N ₂	–	–	–		
Residue %		Air	0	2.7	3.95		
		N ₂	–	–	–		
DTA	100–370 °C (endothermic domain)	$T_{\text{opire}}/^\circ\text{C}$	Air	148.00	100.00	136.00	
			N ₂	139.50	100.00	136.00	
		$T_{ml}/^\circ\text{C}$	Air	314.46	228.50	274.23	
			N ₂	313.89	285.55	276.79	
		$T_{mll}/^\circ\text{C}$	Air	–	321.96	314.39	
			N ₂	–	320.88	318.86	
	370–600 °C (exothermal domain)	$T_i/^\circ\text{C}$	Air	371.74	365.00	379.64	
			N ₂	–	–	–	
		$T_{inf}/^\circ\text{C}$	Air	–	–	502.71	
			N ₂	–	–	534.88	
		$T_m/^\circ\text{C}$	Air	497.83	512.61	508.26	
			N ₂	–	–	–	
$T_f/^\circ\text{C}$	Air	544.29	594.22	590.05			
	N ₂	–	–	–			

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, $W_{\infty}/\%$ weight loss (%), A_{DTA} area of the DTA exothermic peak

Scheme 2 First stage of degradation mechanism—nitrogen elimination for the samples **a**, **b**, and **c**



these diazoaminoderivatives as also mentioned in our previous studies, the nitrogen molecule is responsible for the easiest possible fragmentation of the compounds **a**, **b**, **c** as also confirmed by the TG–DTG analysis.

Under the assumption of the diazoaminoderivatives decomposition starting with the nitrogen elimination, two radical fragments (I and II) might occur (Scheme 2).

The three samples under study, **a**, **b**, and **c**, are noticed to give the same radical fragment I which would suggest that only the substitutes in the radical fragment II affect the thermal stability expressed by the $-\text{C}-\text{N}=\text{N}-$ bond strength. Thus, the compounds **b** and **c** contain in their structure the $-\text{OH}$ group in the *ortho* position with respect to the $-\text{C}-\text{N}=\text{N}-$ group (Scheme 1), that is a favorable position for settling hydrogen bonds between the nitrogen atom and the hydrogen in the phenol $-\text{OH}$ group. Due to the hydrogen bond, the nitrogen elimination is more difficult and that is why the compounds **b** and **c** show higher thermal stability than **a** where such a hydrogen bond is missing. The dimethylamino group, $-\text{N}(\text{CH}_3)_2$, in the radical fragment II in the structure of the sample **a** has a strong electron-releasing effect and the nitrogen elimination is thus easier than from the compounds **b** and **c** which are consequently more stable.

The higher thermal stability of the compound **c** in comparison with **b** might be explained by the presence of the electron-withdrawing $-\text{SO}_3\text{H}$ group in the compound **c**, the radical fragment II, that contributes to the $-\text{C}-\text{N}=\text{N}-$ bond strengthening. Based on these considerations about the structure of the compounds under study and the influence of the substitutes on the $-\text{C}-\text{N}=\text{N}-$ bond the same thermal stability order as found from TG–DTG can be given as:

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

The data in Table 1 show that the temperatures corresponding to the inflexion in the first stage in the endothermic domain for degradation in both air and

nitrogen atmosphere are about the same for the investigated samples suggesting thus the same chemical process to develop as results from TG at a weight loss ($W_t\%$) close to the theoretical one ($W_{\text{exp.}\%}$) for the nitrogen elimination (Table 2).

The temperatures at the maximum degradation rate of the samples degraded in air and in nitrogen within the endothermic domain are the same for every sample and different from one sample to another due to the different substitutes in the radical II (Table 1).

In the exothermic domain for the degradation in air (Scheme 3), the temperatures at the maximum degradation rate from DTG and DTA are close with all the samples which would suggest an exothermic burning reaction of some slightly different molecular fragments (intermediates).

The same degradation mechanism from TG–DTG for every compound in air and in nitrogen atmosphere in the endothermic domain is also supported by the fact that the weight losses in the endothermic domain in air ($W_{\infty}\%$ (endo)) and in nitrogen atmosphere ($W_{\infty}\%$) are close (Table 3).

The TG–DTG–DTA analysis coupled with the FTIR measurements made evident the Gram–Schmidt curves to be identical for degradation in air, endothermic domain, and in nitrogen atmosphere with every sample. The Gram–Schmidt

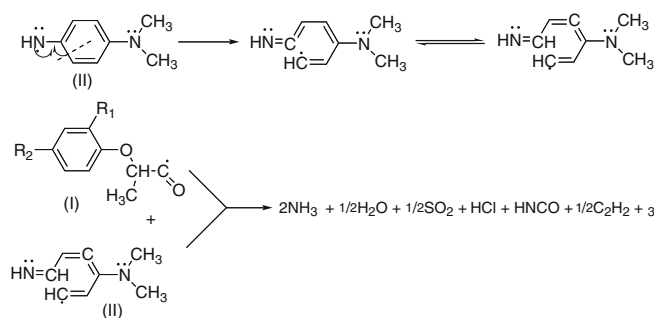
Table 2 Theoretical ($W_t\%$) and experimental ($W_{\text{exp.}\%}$) weight losses of the samples by nitrogen elimination at $T_{\text{inf}}\text{ }^\circ\text{C}$ (stage I), for the degradation of the samples in air and in nitrogen

Sample	$W_{\text{theoretical}}$	$W_{\text{experimental}}$	
		Air	N_2
a	6.58	5.62	6.54
b	6.22	5.87	5.00
c	5.29	4.93	5.03

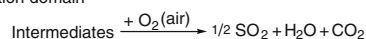
Scheme 3 a Degradation mechanism in endothermic domain, after nitrogen elimination, and in exothermal one for the sample **a. b** Degradation mechanism in endothermic domain, after nitrogen elimination, and in exothermal one for the sample **b. c** Degradation mechanism in endothermic domain, after nitrogen elimination, and in exothermal one for the sample **c**

Sample a:

Endothermic degradation domain

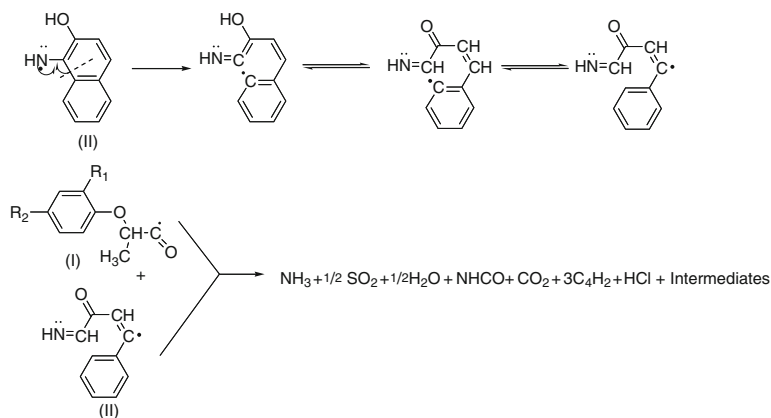


Exothermal degradation domain

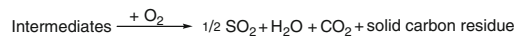


Sample b:

Endothermic degradation domain

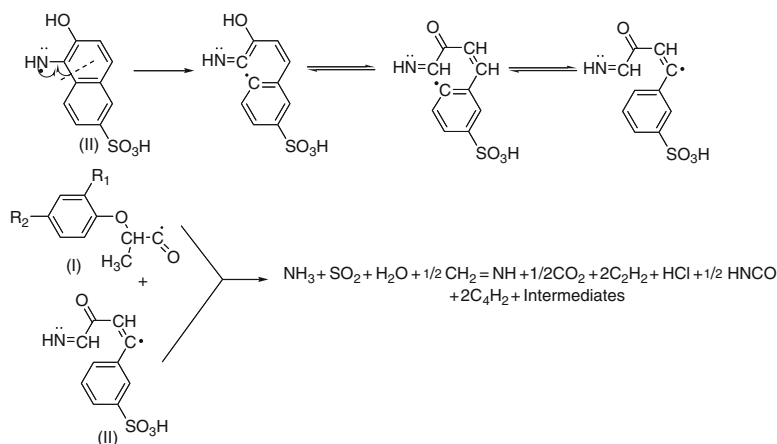


Exothermal degradation domain



Sample c:

Endothermic degradation domain



Exothermal degradation domain

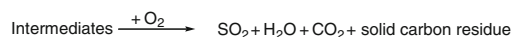


Table 3 Weight losses in nitrogen atmosphere, $W_{\infty}\%$ (N_2), and in air in the endothermic domain, $W_{\infty}\%$ (endo)

Sample	$W_{\infty}\%$ (N_2)	$W_{\infty}\%$ (endo) air
a	77.83	77.62
b	77.94	75.84
c	68.29	63.26

curves for degradation in air are grouped into two temperature domains corresponding to those from TG-DTG-DTA analysis (Figs. 1a–c, 2a–c)

By the FTIR analysis [18–22] of the gases resulting by thermal degradation in air in the endothermic domain and in nitrogen atmosphere and making use of the IR standard spectra [23], the same gaseous species for the same sample were identified and differences were noticed from one sample to another. Thus,

- Sample a: gaseous species: N_2 , NH_3 , H_2O , SO_2 , HCl , $HNCO$, C_2H_2 , C_4H_2
- Sample b: gaseous species: N_2 , NH_3 , H_2O , SO_2 , CO_2 , C_4H_2 , HCl
- Sample c: gaseous species: N_2 , NH_3 , SO_2 , H_2O , $CH_2=NH$, CO_2 , C_2H_2 , HCl , $HNCO$, C_4H_2

The nitrogen eliminated at the degradation beginning in both air and nitrogen atmosphere made evident by TG-DTG (Table 2) cannot be detected by FTIR analysis due to the high nitrogen content in both cases (in air: 70% N_2).

It can be noticed that the nature of the gases resulting by degradation is different from one sample to another which makes evident the influence of the substitute nature on the degradation mechanism.

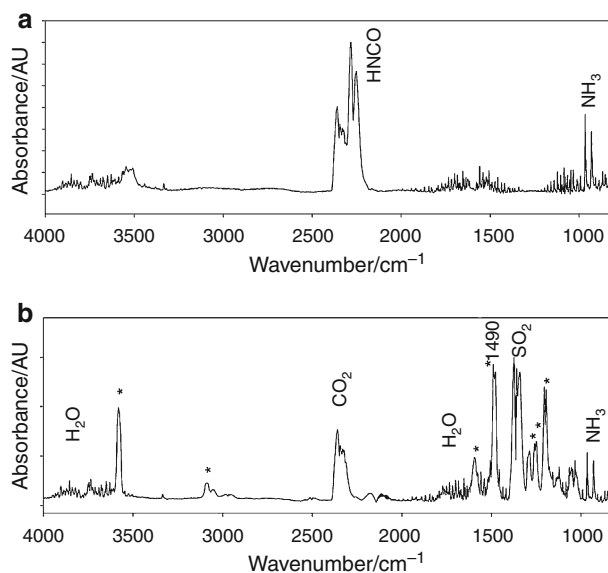
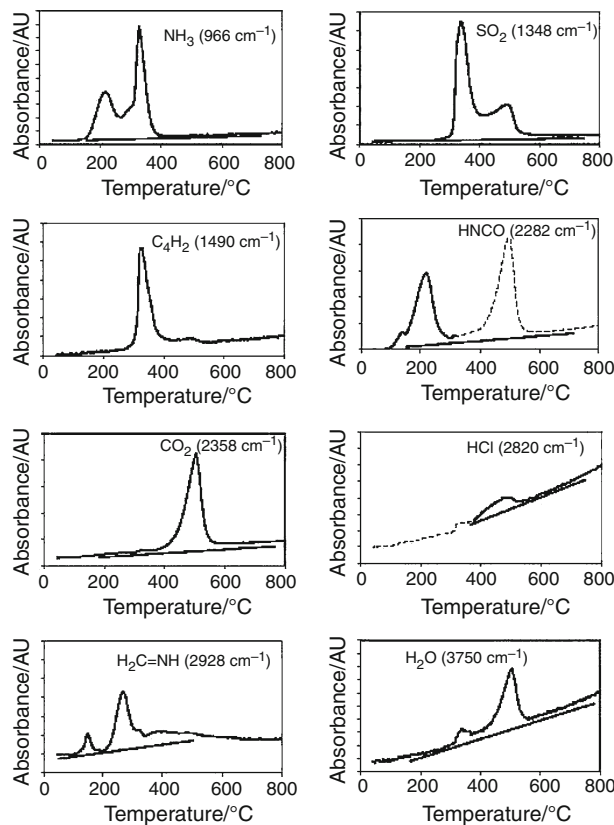
In the exothermic domain, in case of the degradation in air, the following gaseous components resulting by the burning of the solid intermediates formed after the endothermic degradation domain are identified: CO_2 , H_2O , SO_2 .

For exemplification (Figs. 3a, b), the FTIR spectra of the gaseous species resulting by the thermal degradation of the sample a in air and in nitrogen atmosphere at 20.1 min and 24.4 min are depicted:

The IR absorbances in function of temperature for the identified gaseous species are depicted in Fig. 4.

The above-mentioned conclusions are also supported by the 3D-FTIR spectra. The 3D-FTIR spectra of the samples, for degradation in air and in nitrogen atmosphere, are presented in Figs. 5a–c and 6a–c, respectively.

On the basis of the TG-FTIR analysis, correlated with the compound structures, the most plausible mechanism of thermal degradation in air and in nitrogen atmosphere under the conditions of the TG analysis is given in Scheme 3.

**Fig. 3** a FTIR spectrum for gaseous products evolving from sample a (20.1 min). b FTIR spectrum for gaseous products evolving from sample a (24.4 min)**Fig. 4** IR absorbance versus temperature curves of identified evolved gaseous species from samples in air, measured by online-coupled TG-FTIR system (heating rate $10\text{ }^{\circ}\text{C min}^{-1}$; N_2 flow rate 100 mL min^{-1})

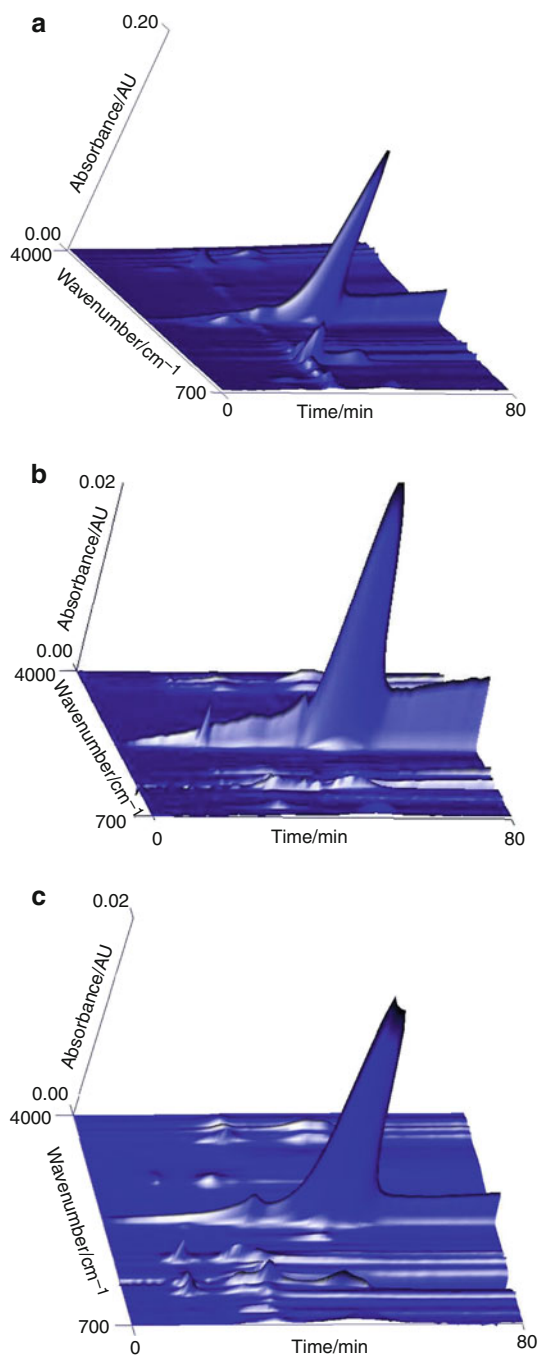


Fig. 5 **a** 3DFTIR spectra obtained for the thermal degradation of the sample **a** in air. **b** 3DFTIR spectra obtained for the thermal degradation of the sample **b** in air. **c** 3DFTIR spectra obtained for the thermal degradation of the sample **c** in air

Conclusions

The comparative study on the thermal degradation in air and in nitrogen atmosphere of three new diazoaminoderivatives by TG-FTIR analysis affords the following conclusions:

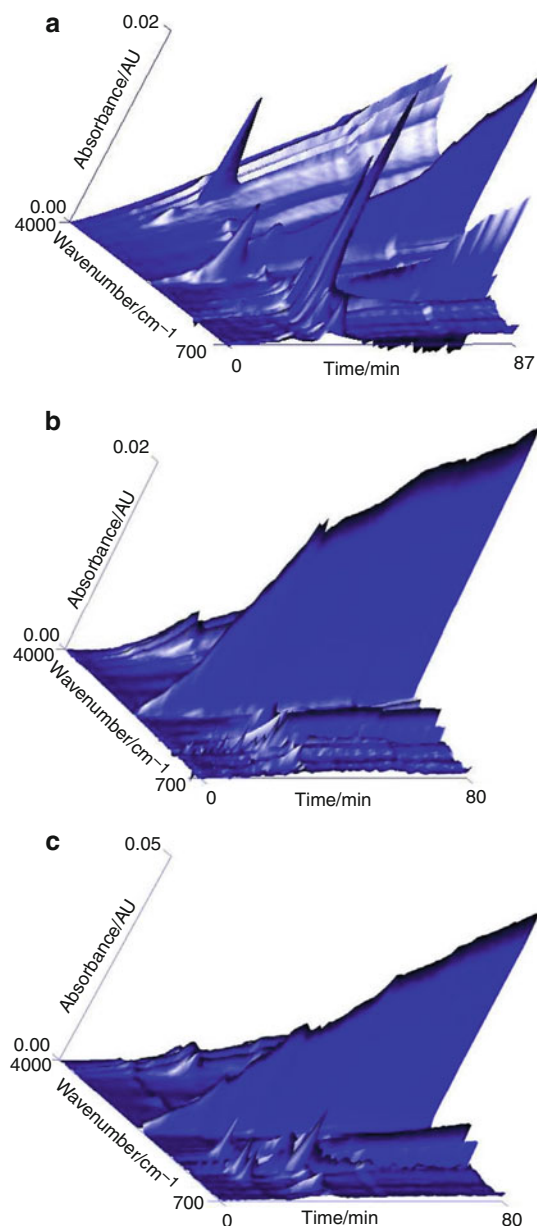


Fig. 6 **a** 3DFTIR spectra obtained for the thermal degradation of the sample **a** in nitrogen atmosphere. **b** 3DFTIR spectra obtained for the thermal degradation of the sample **b** in nitrogen atmosphere. **c** 3DFTIR spectra obtained for the thermal degradation of the sample **c** in nitrogen atmosphere

- 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 are to be found: an endothermic one identical to the case of the degradation under nitrogen atmosphere and the other exothermic which is not to be found with the degradation under nitrogen atmosphere.
- The characteristic temperatures resulting from the TG–DTG–DTA analysis are indicative of a good agreement between the melting points from 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:

c > b > 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 (Gram–Schmidt diagrams for degradations in both air and nitrogen).
- Based on the identification of the gaseous species eliminated by thermal degradation in air and in nitrogen atmosphere in the endothermic domain and in the exothermic domain (degradation in air), as well as on the TG–DTG–DTA analysis data, the most plausible thermal degradation mechanism was advanced for the compounds under study.
- The degradation mechanism in air, in the endothermic domain, was found to be identical to that under nitrogen atmosphere.
- 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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