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# Influence of the aromatic substitutes in the thermal and kinetic behavior of mesoionic compounds of the 1,3-thiazole-5-tiolate system

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#### ABSTRACT

In this work, three mesoionic compounds of the 1,3-thiazole-5-tiolat system were studied, derived from amino acids of the glycerin through 1,3-dipolar cyclo-addition/reversion reaction. The mesoionic compounds were characterized as: MI-1 (mesoionic 2-(4-chlorophenyl)-3-methyl-4-phenyl-1,3-thiazole-5-tiolat); MI-2 (mesoionic 2-(4-chlorophenyl)-3-methyl-4-(4-isopropylphenyl)-1,3-thiazole-5-tiolat) and MI-3 (Mesoionic 2-(4-chlorophenyl)-3-methyl-4-(methoxyphenyl)-1,3-thiazole-5-tiolate). These compounds were characterized by infrared spectroscopy (IR), nuclear magnetic resonance (NMR), thermogravimetry (TG) and differential scanning calorimeter (DSC). Also, the kinetic study of the thermal decomposition by non-isothermal thermogravimetry has been realized, presenting, the kinetic and thermal behavior of these compounds. The DSC curves of the mesoionic compounds MI-1, MI-2, and MI-3 indicated the fusion of two of them followed by a subsequent decomposition. The TG/DTG curves showed that the decomposition of the mesoionic compounds MI-1, MI-2 and MI-3 occurred in several steps.

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# 1. Introduction

Mesoionic compounds are defined as planar five-member heterocyclic betaines with at least one side-chain whose  $\alpha$ -atom is also in the ring plane with dipole moments of the order of 5D [1–5]. A generic representation of the mesoionic compounds of the 1,3thiazolium-5-thiolate system is shown by the Structure 1 where R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> can be alkyl or aryl groups.



Studies show that the mesoionic compounds exhibit a high potential for useful biological activities, such as, antitumor, anti-inflammatory, antimalaric and analgesic [6–8]. Besides the therapeutic applications, nowadays, mesoionics are being stud-

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crislene@pq.cnpq.br, crislene@dema.ufcg.edu.br (C.R. da Silva Morais), athayde-filho@pq.cnpq.br (P.F.d.A. Filho), brunofrlira@hotmail.com (B.F. Lira), ramcos31@yahoo.com.br (M.A.f.d. Souza). ied as promising structures for nonlinear optical devices with application in the storage and transmission of technological information [2,4,9–13]. The main applicability of the mesoionic compounds lies in the large variety of biological activities presented by this kind of betainic compound. One believes that this diversity is related to structural and electronic factors such as: the betainic characteristics which lead to strong interactions with many biomolecules, structural similarity with many active pharmacologic drugs or electrostatic interaction with two complementary positions, such as a protein helice. In view of the fact that no previous results exist on the kinetic and thermal behavior of these compounds, this study aims to study the thermal behavior of three mesoionic compounds of the 1,3-thiazolium-5-thiolate system by infrared spectroscopy (IR) and thermal analysis (TG and DSC), as well as, to determine the kinetic parameters (activation energy, pre-exponential factor and reaction order) using integral mathematical treatments and non-isothermal thermogravimetric analysis.

#### 2. Experimental

#### 2.1. Synthesis of mesoionic compounds

All reagents and solvents were obtained from commercial sources and used as supplied. Mass spectra were obtained on a Finnigan GCQ Mat type quadrupole-ion

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trap spectrometer. IR spectra (KBr) were obtained on a Bruker IFS66 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra (DMSO-d<sub>6</sub> with internal TMS) were recorded on a Varian Unity Plus 300 MHz spectrometer. Elemental analysis was carried out on a PerkinElmer elemental microanalyser. Melting points were determined on a Kofler hot-plate apparatus combined with a Carl-Zeiss microscope and are uncorrected.

Mesoionic compounds (MI) were synthesized according to the methodology described by Athayde-Filho et al. [2] starting from amino acids, obtained through Strecker synthesis (i), that were treated with aroyl chlorides (ii), cyclized for the action of acetic anhydride (iii) and finally submitted to 1,3-dipolar cyclo-addition/reversion with carbon disulphide (iv) (Scheme 1). The structures of compounds were elucidated and compared with the data described in the literature [2,4] through elementary analysis studies, infrared spectroscopy and RMN of <sup>1</sup>H and <sup>13</sup>C. Four mesoionics of the 1,3-thiazolium-5-thiolate system were obtained: 2,4-diphenyl-3-methyl-1,3-thiazolium-5-thiolate (MI-1); 2-(4-chlore-phenyl)-3-methyl-4-phenyl-1,3-thiazolium-5-thiolate (MI-2) and 2-(4-chlore-phenyl)-3-methyl-4-(4-methoxy-phenyl)-1,3-thiazolium-5-thiolate (MI-3).

#### 2.1.1. Preparation of mesoionics compounds-general procedure

The *N*-aroyl-*N*-methyl-*C*-arylglycines (1) were dissolved in Ac<sub>2</sub>O (20 mL) and heated, with stirring, at 55 °C for 15 min. After cooling to ambient temperature, CS<sub>2</sub> (20 mL) was added and the reaction mixture allowed to stand for 48 h. MeOH/H<sub>2</sub>O (1:1) was then added until the mixture became cloudy. After standing for 24 h, the desired products precipitated as orange–red crystals, which were recrystallized from MeOH.

2.1.1.1. 2,4-Diphenyl-3-methyl-1,3-thiazolium-5-thiolate (MI-1). N-benzoyl-N-methyl-C-phenylglycine 5.00 g (19.40 mmol); IR, KBr ( $\nu$  cm<sup>-1</sup>): 3025 ( $\nu$ C<sub>Ar</sub>-H), 2948 ( $\nu$ C-H), 1482 ( $\nu$ N-CH<sub>3</sub>-asymmetric), 1424 ( $\nu$ N-CH<sub>3</sub>-asymmetric), 1291 ( $\nu$ C-S<sup>-</sup> thiol group); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$ =3.64 (s, 3H, H-10), 7.33 (m, 3H-aromatics) and 7.52 (m, 7H-aromatics). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$ =159.8, 140.7, 154.3, 139.1, 131.1, 132.8 (C-7 and C-7'), 129.7, 129.6 (C-11), 129.4, 128.2, 123.8, 40.3; Anal. Calcd for C<sub>16</sub>H<sub>13</sub>NS<sub>2</sub>: C, 53,13; H, 5.82; N, 6.21. Found: C, 53.20; H, 5.70; N, 6.29; yield 51%, m.p. 183–184 °C [recryst. EtOH:H<sub>2</sub>O (1:1, v/v)].

2-(4-chloro-phenyl)-3-methyl-4-phenyl-1,3-thiazolium-5-thiolate (MI-2)—N-(4-chloro-benzoyl)-N-methyl-C-phenylglycine 0.5 g (1.4 mmoles); IR, KBr (ν cm<sup>-1</sup>); 3049 (νC<sub>Ar</sub>(H); 2981 and 2853 (νC(H); 1580, 1468 (νC=C and C=N); 1434 (νC(N, N-CH<sub>3</sub>); 1282 (νC-S<sup>-</sup>, thiol group); 1087 (νC<sub>Ar</sub>(Cl); <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  3.62 (s, 3H; H-10); 7.44 (dd; 1H; H-14); 7.46 (t; 2H; H-13 and 13'); 7.52 (s, H-7 and 7'); 7.52 (s, H-8 and 8') and 7.57 (dd, 2H; H-12 and 12'); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 161.2 (C-5); 152.3 (C-2); 141.2 (C-4); 138.0 (C-9); 131.1 (C-12 and C-12'); 130.7 (C-7 and C-7'); 129.9 (C-8 and C-8'); 129.8 (C-11); 129.3 (C-14); 128.8 (C-13 and C-13'); 125.2 (C-6), 40.5 (C-10). Anal. Calcd for C<sub>16</sub>H<sub>12</sub>CINS<sub>2</sub>, C, 60.46; H, 3.81; N, 4.41; Found: C, 60.82; H, 4.73; N, 4.22; yield 61.3% m.p. 179–181°C [recryst. EtOH:H<sub>2</sub>O (1:1, v/v)].

 $\begin{array}{l} 2\mbox{-}(4\mbox{-}chloro\mbox{-}phenyl)\mbox{-}3\mbox{-}methyl\mbox{-}4\mbox{-}chloro\mbox{-}phenyl)\mbox{-}1,3\mbox{-}thiazolium\mbox{-}5\mbox{-}thiazolium\mbox{-}1\mbox{-}chloc\mbox{-}thiazolium\mbox{-}1\mbox{-}5\mbox{-}thiazolium\mbox{-}thiazolium\mbox{-}1\mbox{-}5\mbox{-}thiazolium\mbox{-}thiazolium\mbox{-}1\mbox{-}5\mbox{-}thiazolium\mbox{-}thiazolium\mbox{-}1\mbox{$ 

131.4, 129.5, 125.5, 122.5, 113.5, 55.3, 40.3; Anal. Calcd for  $C_{17}H_{14}ClNOS_2$ , C, 58.69; H, 4.06; N, 4.03; Found: C, 58.39; H, 3.82; N, 4.20; yield 56%, m.p. 215–217 $^\circ$ C [recryst. EtOH:H\_2O (1:1, v/v)].

#### 2.2. Thermal measurements

Thermogravimetric curves were obtained using a Shimadzu model TGA-50 thermobalance with an alumnae crucible, and with heating rates of  $10 \,^{\circ}$ C min<sup>-1</sup> in a temperature range from ambient 1 to 900  $^{\circ}$ C and under a nitrogen atmosphere with a flow rate of 50 mL min<sup>-1</sup>. The sample mass was  $2.0 \pm 0.5$  mg. The TG curves were analyzed with the aid of the TASYS software from Shimadzu.

The DSC curves were achieved in a SHIMADZU, DSC-50 calorimeter. The analyses were realized in an aluminum crucible with a nitrogen atmosphere, flux  $50 \,\text{mLmin}^{-1}$ , temperature range from ambient 1 to  $500 \,^{\circ}\text{C}$  and heat rates  $10 \,^{\circ}\text{C} \,\text{min}^{-1}$ .

#### 2.3. Spectroscopy

The infrared spectra were achieved in a BOMEM-MICHELSON SERIES instrument, employing KBr pellets and registering amplitude waves ranging from 400 to 4000 cm<sup>-1</sup>.

#### 2.4. Other measurements

The kinetic parameters, activation energy, reaction order and frequency factor were obtained from the thermogravimetric data by the integral methods proposed by Coats and Redfern (CR) [14] and Madhusudanan (MD) [15], and the approximation methods proposed by Horowitz–Metzger (HM) [16] and Van Krevelen et al. (VK) [17]. The kinetic parameters in the non-isothermal heating method were determined according to the Coats and Redfern [14] equation, using the thermal decomposition model suggested by the data obtained in the isothermal heating experiments [18].

#### 3. Results and discussion

#### 3.1. Spectroscopic results

All the products gave satisfactory elemental analyses. In all of the infrared spectra, characteristic bands can be observed of the functional groups, such as, the absorption band of exocyclic tiolat ( $\nu$ C–S<sup>-</sup>) between 1280 and 1291 cm<sup>-1</sup> which certifies the existence of a lateral chain and consequent generation of the mesoionic compound. Table 1 shows the main attributes of the absorption bands, observed in the infrared spectra in the range 4000–400 cm<sup>-1</sup>.

Studies of <sup>1</sup>H NMR of mesoionic compounds are not very informative when there is no hydrogen in the heterocyclic ring, however these are important in the detection of hydrogens in the substituent groups. In contrast, the <sup>13</sup>C NMR spectroscopy is an important tool

Table 1			
Infrared absorption	bands	of mesoionic	compounds.

Compounds	Attributions	Attributions $\nu$ (cm <sup>-1</sup> )							
	C <sub>Ar</sub> -H	C-H (as)	C–H (s)	N-CH <sub>3</sub>	C–S <sup>–</sup>	=C-Cl	С-О-С	C–F	
MI-1	3025	2948		14251482	1291	-	-	-	
MI-2	3049	2981	2853	1434	1282	1087	-	-	
MI-3	3025	2948	-	14241482	1291	-	-	-	

to characterize the structure of mesoionic compounds due to the large difference in electronic densities between the two regions of the betainic ring (positive and negative). This difference in electronic density manifests itself in shielding or deshielding effects of the carbons of the heterocyclic ring and of the carbons of aromatic or aliphatic groups linked to the mesoionic ring. The three peaks at ca. 160, 150, and 140 ppm are attributed to C5, C2, and C4 respectively (see Scheme 1). The reason that C4 is at high field compared with C5; although both are in the negative region of the mesoionic ring can be related to the significant partial double bond character of the carbon-thiolate bond (C5-S5). The methylic carbon linked to N-3 is characterized by a peak at 40 ppm and the methylic protons have chemical shifts around 3.60 ppm, there is a down-field shift as a result of the positive charge on N3. The carbon atoms with chemical shift at low field, 159.6 ppm, are affected by deshielding effects caused by the existence of the methoxy group.

The <sup>13</sup>C NMR (APT, 50 MHz, DMSO-d6) study of the compound MI-1 showed that the carbons of the mesoionic ring have chemical shifts of 154.3; 140.7 and 159.8 ppm assigned, respectively, to C2, C4 and C5 (see Scheme 1). The carbon C10 has chemical shifts of 40.7 ppm, while the aromatic carbons have chemical shifts of 139.1 (C-9), 131.1 (C-12 and C-12'), 132.8 (C-7 and C-7'), 129.7 (C-8 and C-8'), 129.6 (C-11), 129.4(C-14), 128.2(C-13 and C-13'), and 123.8 ppm (C-6).

The <sup>1</sup>H NMR (200 MHz, DMSO-d6) spectrum of MI-1 shows two hydrogen signals. Of these, one intense singlet was observed in the aliphatic region with an integral of 3H for the hydrogens H10 of the methyl group in 3.64 ppm. There was also a signal between 8.27 and 7.23 assigned to the eight aromatic hydrogens.

For compound MI-2 we observed a similar chemical behavior. The <sup>13</sup>C NMR (APT, 50 MHz, DMSO-d6) spectrum showed the carbons of the mesoionic ring in chemical shifts of 152.3; 141.2 and 161.2 for C2, C4 and C5, respectively (see Scheme 1). Carbon C10 shows chemical shifts that are compatible with the *N*-methyl group in 40.5. The aromatic carbons have chemical shifts of 138.0 (C-9), 131.1 (C-12 and C-12'), 130.7 (C-7 and C-7'), 129.9 (C-8 and C-8'), 129.8 (C-11), 129.3 (C-14), 128.8 (C-13 and C-13'), and 125.2 ppm (C-6).

The <sup>1</sup>H NMR (200 MHz, DMSO-d6) spectra of MI-2 were observed as one intense singlet in the aliphatic region with an integral of three hydrogen assigned to the *N*-methyl group of the heterocyclic ring in 3.69 ppm. In the region between 8.34 and 7.07 ppm we observed corresponding signals for the nine aromatic hydrogens.

For compound MI-3 we observed a similar chemical behavior. The <sup>13</sup>C NMR (APT, 50 MHz, DMSO-d6) spectrum showed the carbons of the mesoionic ring in chemical shifts of 151.1; 141.2 and 161.2 for C2, C4 and C5, respectively (see Scheme 1). Carbons C10 and C15 show chemical shifts that are compatible with the *N*-methyl group in 40.8 and the methoxy group in 55.3. The aromatic carbons have chemical shifts of 136.2 (C-9), 132.6 (C-12 and C-12'), 131.4 (C-7 and C-7'), 129.5 (C-8 and C-8'), 125.5 (C-6), 122.5 (C-11), and 113.5 ppm (C-13 and C-13').

The <sup>1</sup>H NMR (200 MHz, DMSO-d6) spectrum of MI-3 showed two intense singlets in the aliphatic region with an integral of six hydrogens, three hydrogens were assigned to the *N*-methyl group

of the heterocyclic ring in 3.66 ppm and three were assigned to the methoxy group in 3.82 ppm. In the region between 8.34 and 7.07 ppm we observed corresponding signals for the eight aromatic hydrogens.

The results above are in agreement with the results observed by Athayde-Filho et al. [4,5].

#### 3.2. Thermal behavior

The mesoionic DSC curves for MI-1 and MI-2 (Fig. 1) present endothermic peaks at 185.5 and 170.7 °C (respectively) immediately followed by exothermic peaks at 192.1 °C (MI-1) and 175.7 °C (MI-2), characteristics of a fusion process followed by the compounds decomposition. After that, two endothermic bands can be observed with a maximum at 266.8 and 296.1 °C, for MI-1 and an endothermic band with a maximum at 265.9 °C (MI-2), a characteristic of thermal decomposition. The mesoionic DSC curve presents five endothermic bands with maximum at 43.6, 146.6, 191.6, 207.4 and 335.2 °C. The first band refers to the loss of humidity of the compound which can be confirmed through the infrared spectra. The other bands refer to its own decomposition.

Figs. 2–4 present TG/DTG curves of the mesoionic compounds (heat rate  $1.0 \circ C \min^{-1}$ ). It can be observed that the MI-1 mesoionic compound present only one decomposition step. The MI-2 and MI-3 present 5 and 4 decomposition steps, respectively.

Table 2 presents the results obtained in TG/DTG curves of the studied compounds. The experimental mass loss (%), the temperature ranges ( $^{\circ}$ C) and the attributions referred to each decomposition step of the mesoionic compounds is defined in the table.

For MI-1 only one decomposition step can be observed with mass loss of 99.1% in a temperature range between 191 and 347 °C. The MI-2 compound presents 5 decomposition steps with mass loss of 6.6%; 71.9%; 8.1%; 6.5% and 3.1% for the temperature ranges 152–210; 210–354; 354–435; 435–577 and 634–787 °C, respectively. It can be observed that the higher mass loss occurred in the



Fig. 1. DSC curves of the mesoionic compounds MI-1, MI-2 and MI-3 obtained using a heating rate of  $10 \,^\circ$ C min<sup>-1</sup>.

#### Table 2

Thermal decomposition data for mesoionic compounds at 10 °C min<sup>-1</sup>.

Compounds	Stage	Temperature range (°C)	Mass loss (%)	Species lost
MI-1	1	191–347	99.1	$C_8H_8N + C_8H_5S_2$
	Residue	>347	0.9	-
MI-2	1	152–210	6.6	CH <sub>3</sub>
	2	210-354	71.9	$C_8H_7CIN + CS_2$
	3	354-435	8.1	$C_2H_2$
	4	435–577	6.5	$C_2H_2$
	5	634–787	3.1	С
	Residue	>787	3.8	-
MI-3	1	138–227	3.7	CH <sub>3</sub>
	2	227-379	70.1	$C_7H_5CIN + C_3H_5 + CS_2$
	3	380-425	13.6	$C_4H_4$
	4	495-871	6.8	$C_2H_2$
	Residue	>871	5.8	-

Table 3

Kinetic parameters of compounds MI-1, MI-2 and MI-3 calculated starting from the non-isothermal thermogravimetric data (heating rates of 10°C min<sup>-1</sup>).

Compounds	Stage	Parameters	Methods			
			CR	MD	HM	VK
MI-1	1	n	0.12	0.32	0.34	0.23
		Ea	91.41	95.01	115.21	98.00
		Α	$1.74 \times 10^{6}$	$4.51 \times 10^{6}$	$4.20  imes 10^6$	$2.46 \times 10^{12}$
		r	1.000	1.000	0.999	0.978
MI-2	2	n	0.52	0.51	0.68	0.56
		Ea	98.60	98.53	120.31	120.31
		Α	$5.07  imes 10^6$	$5.37  imes 10^6$	$6.47 \times 10^8$	$4.79\times10^{12}$
		r	1.000	1.000	0.999	0.981
MI-3	2	n	0.50	0.56	0.74	0.69
		Ea	113.86	116.63	140.70	132.44
		Α	$4.30  imes 10^7$	$8.54 imes10^7$	$1.26\times10^{10}$	$8.32\times10^{14}$
		r	1.000	1.000	0.999	1.000

 $\phi$  = heat rate (°C/min); *n* = reaction order; *r* = linear correlation coefficients;  $E_a$  = activation energy (kJ mol<sup>-1</sup>); A = frequency (s<sup>-1</sup>); CR = Coats-Redfern; MD = Madhusudanam et al.; HM = Horowitz-Metzger and VK = Van Krevelen.

second decomposition step. For MI-3 four decomposition steps can be observed with mass loss of 3.7%; 70.1%; 13.6% and 6.8% for the temperature ranges138–227; 227–379; 380–425 and 495–871 °C, respectively. In this case as well a higher mass loss occurred in the second decomposition step. Based on the mesoionic decomposition temperatures, the following increasing order of thermal stability can be proposed: MI-3 < MI-2 < MI-1.

## 3.3. Kinetic studies of non-isothermal decomposition

Kinetic studies of non-isothermal decomposition were realized using the best experimental conditions according to the relation between the thermogravimetric profile and the heating rate, using decomposed fraction ( $\alpha$ ) from 0.15 to 0.85. The kinetic parameters how reaction order (n), apparent activation energies ( $E_a$ ) and frequency factor (A) for the stage considered more significant in each



Fig. 2. TG/DTG curve of the mesoionic MI-1 obtained using a heating rate of  $10\,^\circ C\,min^{-1}.$ 



Fig. 3. TG/DTG curve of the mesoionic MI-2 obtained using a heating rate of  $10\,^\circ C\,min^{-1}.$ 

# Table 4

Kinetic parameters determined using non-isothermal thermogravimetric method of Coats-Redfern's equation for  $\phi = 10^{\circ}$ C min<sup>-1</sup>.

Compounds	Stage	Parameters	Models		
			R1	D1	D2
MI-1	1	Ea	87.54	184.04	203.65
		Α	$6.82  imes 10^5$	$1.20 \times 10^{15}$	$6.30  imes 10^{16}$
		r	0.9997	0.9998	0.9999
		S	0.0098	0.0191	0.0153
		Ea	97.79	103.59	200.68
MI-2	2	Α	$2.10\times10^{6}$	$5.46\times10^{6}$	$1.85\times10^{15}$
		r	0.9999	0.9998	0.9999
		S	0.0036	0.0089	0.0135
		Ea	102.12	108.16	209.32
MI-3	2	Α	$3.65\times10^{6}$	$9.76\times10^{6}$	$5.40\times10^{15}$
		r	0.9999	0.9998	0.9999
		S	0.0051	0.0102	0.0151

 $\phi$  = heat rate (°C/min); r = linear correlation coefficients;  $E_a$  = activation energy (kJ mol<sup>-1</sup>); A = frequency (s<sup>-1</sup>) and s = standard deviation.



Fig. 4. TG/DTG curve of the mesoionic MI-3 obtained using a heating rate of  $10\,^\circ\text{C}\,min^{-1}.$ 

compound, are listed in Table 3. The apparent activation energy for approach methods of Horowitz-Metzger and Van Krevelen are higher than those for integral methods of Coats-Redfern and Madhusudanan.

Hence, the matching of these activation energy values suggests the following decreasing order of thermal stability: MI-3 < MI-2 < MI-1, therefore we will consider the stage most significant. The kinetic models that better described the thermal decomposition reaction for the mesoionic compounds were R1 and R2 (Table 4).

R1 model indicates that the mechanism is controlled by onedimensional phase-boundary reaction (zero order) and is defined by the function  $g(\alpha)=1-(1-\alpha)$ . R2 model indicates that the mechanism is controlled by phase-boundary reaction (cylindrical symmetry) and is defined by the function  $g(\alpha)=2[1-(1-\alpha)^{1/2}]$ , indicating a mean reaction order [13].

# 4. Conclusion

The DSC curve of the mesoionic compounds MI-1 and MI-2 indicates that they suffer a fusion process followed by a decomposition process. This mechanism was not observed in the case of MI-3 mesoionic that presented only decomposition events.

Thermal decomposition of the mesoionic compounds, in nitrogen atmosphere, occurs in various stages. According to the thermogravimetric curves and kinetic studies, the order of thermal stability was as follows: MI-3 < MI-2 < MI-1. The kinetic parameters obtained by approximation and integral methods were satisfactory and presented good correlation. Generally, the activation energy values obtained using the integral methods are lower than the values obtained by the approximation methods. The kinetic models that better described the thermal decomposition mechanisms, obtained by the non-isothermal method were R1 (MI-1) and R2 (MI-2 and MI-3) (based on geometric models).

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