J Therm Anal Calorim (2009) 97:437–441
DOI 10.1007/s10973-009-0082-8

A kinetic study of the thermal decomposition of mesoionic compounds within scope of its application in nonlinear optical devices

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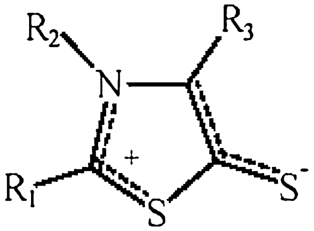
ICTAC2008 Conference

Abstract The mesoionic compounds are pentagonal heterocyclic betaines with their potential use mainly in the pharmacology field due to the diversity of their biological activities. Their exceptional electric properties lead the compounds to be investigated in the field such as the nonlinear optical devices. In this study, five mesoionic compounds of the 1,3-thiazole-5-thiolate system had been synthesized from amino acids derived from glycine through 1,3-dipolar cycloaddition/cycloreversion reaction. The compounds were characterized by the use of infrared spectrometry, thermogravimetry and differential scanning calorimetry techniques. Thermal stability of each structure was determined and characterized by the kinetic study of the thermal decomposition by non-isothermal thermogravimetry. The DSC curves for MI-1, MI-2, MI-3, MI-4, and MI-5 demonstrated their fusion and subsequent decomposition with the exception of MI-3, which presented only decomposition stages. The kinetic models that better described the thermal decomposition mechanism of the mesoionic compounds achieved by the non-isothermal methods were R1, R2 and R3 (based on the geometric models).

Keywords Kinetic · Mesoionic Compounds · Thermal analysis

Introduction

Mesoionic compounds are defined as planar five-member ring betaines with at least one side-chain whose α-atom is in the same surface and with dipole moments of the order of 5D [1–5]. A generic representation of mesoionic compounds of the 1,3-thiazolium-5-thiolate system is shown by structure 1 where R1, R2 and R3 can be alkyl or aryl groups.



Studies show that the mesoionic compounds exhibits a high potential of useful biological activities, such as antitumor, anti-inflammatory, antimalaric, and analgesic [6–8]. Besides the therapeutic applications, nowadays, the mesoionics are being studied as promising structures for nonlinear optical devices with application in storage and transmissions of technological information [9–13].

The aim of this study is to investigate the thermal behavior of five mesoionic compounds of the 1,3-thiazolium-5-thiolate system by the use of infrared spectroscopy (IR) and thermal analysis (TG—by the non-isothermal

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method and DSC), as well as to determine the kinetic parameters (activation energy, pre-exponential factor and reaction order) using integral mathematical treatments.

Experimental

Synthesis of mesoionic compounds

Compounds were synthesized according to the methodology described by De Athayde-Filho and Morais [12, 13] starting from aminoacids, obtained from the synthesis of Strecker (i), that were subsequently treated with aroyl chlorides (ii), cyclized for the action of the acetic anhydride (iii) and finally submitted to a reaction of cycloaddition/reversion 1,3-dipolar with carbon disulphide (iv). The compounds' structures were elucidated and compared with the data described in the literature [12, 13] by the elementary analysis studies, infrared spectroscopy and ^{1}H and ^{13}C NMR. Four mesoionics of the 1,3-thiazolium-5-thiolate system were obtained. The mesoionic compounds were characterized as: Mesoionic 2,4-diphenyl-3-methyl-4-phenyl-1,3-thiazole-5-thiolate (MI-1); Mesoionic 2-(4-chlorophenyl)-3-methyl-4-phenyl-1,3-thiazole-5-thiolate (MI-2); Mesoionic 2-(4-chlorophenyl)-3-methyl-4-(4-isopropylphenyl)-1,3-thiazole-5-thiolate (MI-3), Mesoionic 2-(4-chlorophenyl)-3-methyl-4-(4-methoxyphenyl)-1,3-thiazole-5-thiolate (MI-4) and Mesoionic 2-(4-trifluoromethylphenyl)-3-methyl-4-(4-methoxyphenyl)-1,3-thiazole-5-thiolate (MI-5).

Infrared spectroscopy

The infrared spectra were recorded by using Bomem-Michelson Series instrument, employing KBr pellets and registering amplitude waves ranging from 400 to 4,000 cm^{-1}.

Thermal measurements

Thermogravimetric curves were obtained using a Shimadzu model TGA-50 thermobalance with an aluminium crucible, and at heating rate of 10 °C min^{-1} in a temperature range from ambient to 900 °C and in nitrogen atmosphere with a flow rate of 50 mL min^{-1}. The sample mass was 2.0 ± 0.5 mg. The TG curves were analyzed with the aid of the TASYS software from Shimadzu. The DSC curves were registered in a SHIMADZU, DSC-50 calorimeter. The analysis was conducted in an aluminum crucible in nitrogen atmosphere, flux 50 mL min-1, temperature range from ambient to 500 °C and heating rate of 10 °C min^{-1}.

Kinetic study

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

Results and discussion

Table 1 shows the main attributions of the absorption bands, observed in the infrared spectra registered within range from 4,000 to 400 cm^{-1}. In all of the infrared spectra characteristic bands of the functional groups can be observed, such as, absorption band of exocyclic tiolat

Table 1 Infrared absorption bands of mesoionic compounds

Compounds	Attributions ν(cm^{-1})							
	C_{Ar}–H	C–H(as)	C–H(s)	N–CH_3	C–S$^-$	=C–Cl	C–O–C	C–F
MI-1	3,025	2,948		1,425 1,482	1,291	–	–	–
MI-2	3,049	2,981	2,853	1,434	1,282	1,087	–	–
MI-3	3,025	2,948	–	1,424 1,482	1,291	–	–	–
MI-4	3,043 3,007	2,989	2,831	1,433	1,280	1,098	1,251	–
MI-5	3,033 3,013	2,981	2,898 2,839	1,451	1,287	–	1,033	1,331 1,136

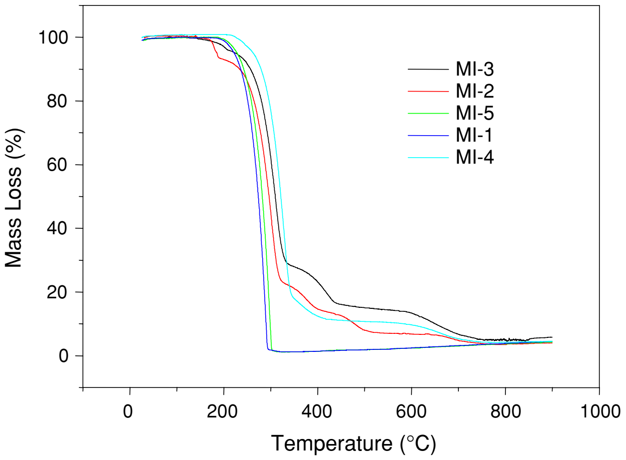

Fig. 1 TG curves of the mesoionics compounds obtained using a heating rate of 10 °C min^{-1}

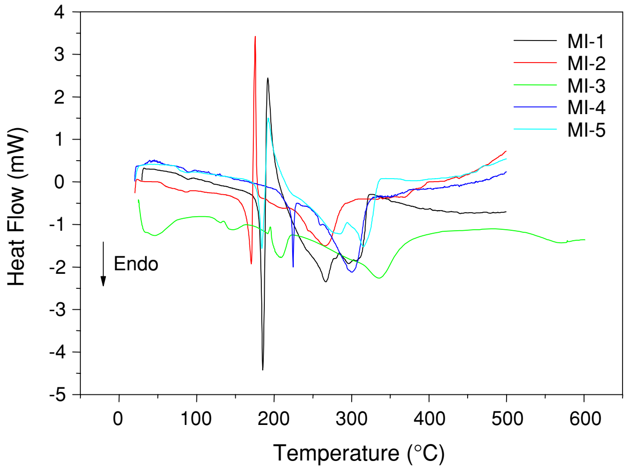

Fig. 2 DSC curves of the mesoionic compounds

(υC–S$^-$) between 1,280 and 1,291 cm^{-1} which certifies the existence of a lateral chain and consequent generation of the mesoionic compound. These results match the ones found by De Athayde-Filho and Lira [4, 5].

Thermal behavior

Thermogravimetric curves of mesoionic compounds are presented in Fig. 1. It can be observed that thermal decomposition process of MI-1 and MI-5 is characterized by only one-step mass loss, while the decomposition process of MI-2, MI-3, and MI-4 include five, four, and two steps of mass loss, respectively. Initial temperatures of decomposition process of compounds, obtained from non-isothermal thermogravimetric curves, are presented in Table 2.

According to the initial temperatures of decomposition process of compounds, the following stability order can be suggested: MI-3 < MI-2 < MI-5 < MI-1 $\leq$ MI-4.

The mesoionic DSC curves MI-1 and MI-2 (Fig. 2) present endothermic peaks at 186 and 171 °C, respectively, immediately followed by exothermic peaks at 192.1 °C (MI-1) and 176 °C (MI-2), which is characteristic of a fusion process followed by the compounds decomposition. Afterwards, two endothermic bands with a maximum at 267 and 296 °C, for the MI-1 can be observed, and an endothermic band with a maximum at 266 °C (MI-2), which represents thermal decomposition. The mesoionic MI-3 DSC curve presents five endothermic bands with maxima at 44, 147, 192, 207, and 335 °C. The first band refers to the loss of humidity of the compound which can be confirmed by the infrared spectra. The other bands refer to its self decomposition.

The mesoionic MI-4 DSC curve present one endothermic peak at 225 °C—characteristics of a fusion process and one bands with a maximum at 301 °C referring to thermal decomposition.

Table 2 Thermal decomposition data for mesoionics compounds at 10 s°C min^{-1}

Compounds	Stage	Temp. range (°C)	Mass-loss (%)	Species lost
MI-1	1	191–347	99.1	$C_8H_8N + C_8H_5S_2$
MI-2	1	152–210	6.6	CH_3
	2	210–354	71.9	$C_8H_7ClN + CS_2$
	3	354–435	8.1	C_2H_2
	4	435–577	6.5	C_2H_2
	5	634–787	3.1	C
MI-3	1	138–227	3.7	CH_3
	2	227–379	70.1	$C_7H_5ClN + C_3H_5 + CS_2$
	3	380–425	13.6	C_4H_4
	4	495–871	6.8	C_2H_2
MI-4	1	193–435	89.6	$C_8H_7ClN + CH_3OH + CS_2 + C_4H_4$
	2	436–777	7.1	C_2H_2
MI-5	1	189–359	98.9	$C_9H_7F_3N + CH_3OH + CS_2 + C_6H_6$

The mesoionic DSC curves MI-5 present one endothermic peak at 184 °C immediately followed by exothermic peak at 192 °C—characteristics of a fusion process followed by the compounds' decomposition. The other bands at 285 and 315 °C refer to its self decomposition.

Kinetic study

Thermal decomposition kinetic study of reactions of compounds enables was conducted in the best experimental conditions according to the relation between the thermogravimetric profile and the heating rate. The decomposed fraction (α) from 0.15 to 0.85 was used. The evaluation of the kinetics parameter as: reaction order (n), apparent activation energy (Ea) and frequency factor (A) for the first and second stage are considered to be more significant in each compound, and are listed in Table 3. The apparent activation energy for approach methods of Horowitz-Metzger and Van Krevelen are larger than those for integral methods of Coats-Redfern and Madhusudanan.

In this way, the matching of these values of activation energy suggests the following decreasing order of thermal stability for the first stage: MI-3 < MI-5 < MI-2 < MI-1 < MI-4.

The kinetic models that described the thermal decomposition reaction more for the mesoionic compounds precisely were R1, R2 and R3 (Table 4).

The R1 model indicate that the mechanism is controlled by one-dimensional phase-boundary (zero order) and is defined by the function $g(\alpha) = 1 - (1 - \alpha)$. The R2 model indicate 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. The at last the R3 model indicate that the mechanism is controlled by tree-dimensional phase-boundary (spherical symmetry) and is defined by the function $g(\alpha) = 2[1 - (1 - \alpha)2/3]$ [16].

Table 3 Kinetic parameters of mesoionic compounds calculated starting from the dynamic thermogravimetric data in heating rates of 10 °C min^{-1}

Compounds	Parameters	Methods			
		CR	MD	HM	VK
MI-1	n	0.12	0.32	0.34	0.23
	E_a	91.41	95.01	115.21	98.00
	A	1.74×10^6	4.51×10^6	4.20×10^6	2.46×10^{12}
	r	1.000	1.000	0.999	0.978
MI-2	n	0.52	0.51	0.68	0.56
	E_a	98.60	98.53	120.31	120.31
	A	5.07×10^6	5.37×10^6	6.47×10^8	4.79×10^{12}
	r	1.000	1.000	0.999	0.981
MI-3	n	0.50	0.56	0.74	0.69
	E_a	113.86	116.63	140.70	132.44
	A	4.30×10^7	8.54×10^7	1.26×10^{10}	8.32×10^{14}
	r	1.000	1.000	0.999	1.000
MI-4	n	0.05	0.09	0.21	0.17
	E_a	88.32	89.63	110.36	101.41
	A	5.97×10^5	9.10×10^{15}	9.36×10^8	3.81×10^{12}
	r	1.000	1.000	0.999	1.000
MI-5	n	0.30	0.40	0.65	0.76
	E_a	95.29	98.87	124.98	124.98
	A	1.50×10^6	3.71×10^6	8.89×10^8	3.98×10^{15}
	r	1.000	1.000	0.999	1.000

Table 4 Kinetic parameters determined using dynamic thermogravimetric method of Coats–Redfern's equation for $\phi = 10$ °C min^{-1}

Parameters	Compounds				
	MI-1	MI-2	MI-3	MI-4	MI-5
E_a(kJ.mol^{-1})	87.54	97.79	102.12	120.75	86.79
A(s^{-1})	6.82×10^5	2.10×10^6	3.65×10^6	6.62×10^7	4.15×10^5
R	0.9997	0.9999	0.9999	0.9999	0.9999
Model	R1	R2	R2	R3	R1

Conclusions

The TG curves indicate that the decomposition of MI-1 and MI-5 compounds occurred in a single step, while the decompositions of MI-2, MI-3, and MI-4 occur in several steps. According to the thermogravimetric analysis, the mesoionic compounds present the following increasing stability order: MI-3 < MI-2 < MI-5 < MI-1 < MI-4. The kinetic models that better described the thermal decomposition mechanism of the mesoionic compounds obtained by the non-isothermal methods were R1, R2, and R3 (based on the geometric models).

Acknowledgements The authors acknowledge UEPB, UFPB, and UFCG and for scholarship and financial support of this work.

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