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THERMAL ANALYSIS STUDY OF IMIDAZOLINIUM AND SOME BENZIMIDAZOLIUM SALTS BY TG

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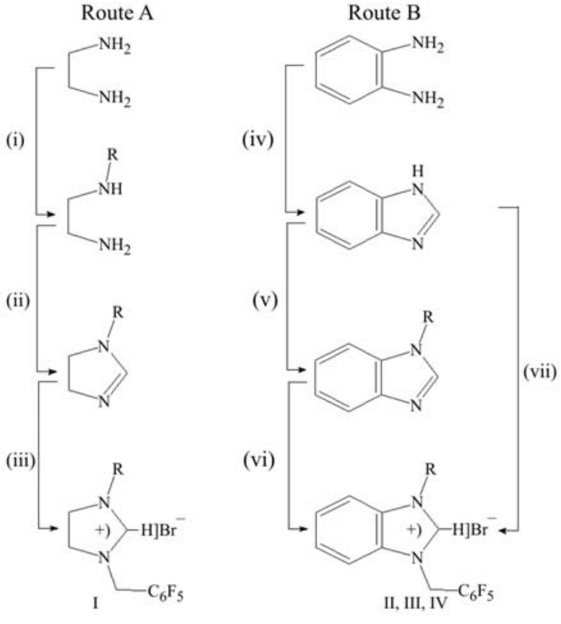
The imidazolinium and benzimidazolium bromide salts with pentafluor substituents on N atom were synthesized. The structures of imidazolinium and benzimidazolium bromide salts obtained were conformed by ^{1}H and ^{13}C NMR, ^{19}F NMR and elemental analysis. It was found that pyrolytic decomposition occurs with melting in salts. The imidazolinium and benzimidazolium bromide salts were studied by TG-DTG and DTA from ambient temperature to 1000°C in nitrogen atmosphere. The decomposition occurred mainly in one stage and the values of activation energy E, frequency factor A, reaction order n, enthalpy change $\Delta H^{\#}$, entropy change $\Delta S^{\#}$ and Gibbs free energy $\Delta G^{\#}$, of the thermal decomposition were calculated by means of Coats–Redfern (CR), MacCallum–Tanner (MC) and van Krevelen (vK) methods. The activation energy value obtained by CR and MC methods were in good agreement with each other while those obtained by vK were found to be 10–12 kJ mol^{-1} larger.

Keywords: *activation energy, benzimidazolium salt, imidazolinium salt, thermal decomposition*

Introduction

N-heterocyclic carbenes (NHC) are becoming substantial structure unit for many organometallic compounds and homogeneous catalyst, but only little attention has been paid to the synthesis of NHC derivatives with fluorophilic properties. NHC complexes with fluorinated substituents are rare [1–5]. This simulated our aim in the synthesis of NHC with C_4–C_5 saturated and pentafluor substitutient(s) on N atom(s). Fluorine, the only element capable of mimicking hydrogen by virtue of comparable size (isosterism) may not only include very specific properties to molecules do to its electron-withdrawing power, but also confer metabolic stability and in addition, enhance the lipophilicity and solubility in *sc*CO_2. On the other hand, pentafluorobenzyl bromide is commercially available and relatively cheap alkyl halide. Thus, this $BrCH_2C_6F_5$, is appeared to us to be ideal reagent for fine-tuning properties of NHC derivatives.

The non-isothermal thermogravimetry (TG) with a linear temperature growth is a method frequently used to characterize materials from their thermal behavior standpoint. In addition, it enables to determine apparent kinetic parameters of heterogeneous reactions (the reaction order n, the activation energy E and the frequency factor A). Considerable attention is paid to the kinetic parameters calculation from TG curves. New calculation methods are still being published [6–10]. A number of papers are devoted to comparing these



Compound	R
I	CH_2–Mes
II	CH_2–Mes
III	CH_2–Ph
IV	CH_2–C_6F_5

Scheme 1 Convenient synthetic routes to imidazolinium and benzimidazolium salts. Reagents and conditions: *(i)* Li, 2,4,6-trimethylbenzyl chloride, PhMe, 110°C; *(ii)* N,N-dimethylformamide dimethylacetal, 120°C; *(iii)* $C_6F_5CH_2Br$, PhMe, 110°C; *(iv)* formic acid, reflux, 10% NaOH; *(v)* KOH, RX, PhMe, r.T; *(vi)* $C_6F_5CH_2Br$, PhMe, 110°C; *(vii)* KOH, $2C_6F_5CH_2Br$, PhMe, 110°C

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methods [11] or to their critical assessment [12]. Strezov [13] was investigated using calorimetric technique the effect of heating rate on the thermal properties of coal. Also, Kök [14–16] was estimated the thermal analysis and kinetics of several coal and oil shale samples by using the same method based on the single heating rate. On the other hand, thermal studies of imidazole and benzimidazole derivatives are rare in literature. Labádi [17] has investigated the thermal stabilities of the mixed ligand complexes with imidazole. The complexes of clotrimazole with cyclodextrins have been studied by Taneri *et al.* [18] using the various thermoanalytical methods. Also, the physicochemical properties of the several metal complexes with salicylidene-2-aminobenzimidazole were investigated by Mohamed *et al.* [19] using thermal and elemental analytical methods. Yeşilel [20] has investigated the thermal behavior of orotic acid complexes of several metals with imidazole in an air atmosphere with TG/DTG and DTA.

In this study, the imidazolinium and benzimidazolium bromide salts with pentafluorobenzyl substituents on N atom were synthesized. The structures of imidazolinium and benzimidazolium bromide salts obtained were conformed by ^{1}H and ^{13}C NMR, ^{19}F NMR and elemental analysis. The thermal behavior, kinetic and thermodynamic parameters of salts were investigated and the values of activation energy *E,* frequency factor *A*, reaction order *n*, of the thermal decomposition were calculated by means of CR [21], MC [22] and vK [23].

Experimental

Materials

Pentafluorobenzyl bromide, o-phenylene diamine, benzyl chloride, N,N-dimethylformamide dimethylacetal, and 2,4,6-trimethylbenzyl chloride were obtained from Aldrich. Formic acid and KOH were obtained from Fluka. All manipulation was performed under argon atmosphere using standard Schlenk Techniques.

Synthesis of 1-pentafluoro-benzyl-3-(2,4,6-trimethylbenzyl) imidazolinium bromide, **I**

A mixture pentafluorobenzyl bromide (1.73 g; 6.62 mmol) and 1-(2,4,6-trimethylbenzyl)imidazolidine (1,33 g; 6.62 mmol)was refluxed in toluene (10 mL) for 2 h. Volume of the solution reduced to ca. 3–4 mL under vacuum. Diethyl ether was added to the solution and filtered. Remaining white precipitate was dissolved in methanol (2 mL) and diethyl ether was added (10 mL). Obtained colorless crystals were filtered and dried under vacuum.

Synthesis of 1-pentafluoro-benzyl-3-(2,4,6-trimethylbenzyl) benzimidazolium bromide, **II**

This salt was synthesized according to literature methods [2].

Synthesis of 1-benzyl-3-pentafluorobenzyl-benzimidazolium bromide, **III**

This salt was synthesized according to literature methods [5].

Synthesis of 1,3-bis(pentafluorobenzyl)benzimidazolium bromide, **IV**

Benzimidazole (0.59 g; 5 mmol) and KOH (0.28 g; 5 mmol) was added in toluene (15 mL) and stirred at room temperature for 1 h. Then pentafluorobenzyl bromide (2.61 g; 10 mmol) added into mixture and refluxed for 2 h. Volume of the solution reduced to ca. 3–4 mL. Diethyl ether was added to the solution and filtered. Remaining white precipitate was dissolved in methanol (4 mL) and diethyl ether was added (15 mL). Obtained colorless crystals were filtered and dried under vacuum.

Methods

^{1}H and ^{13}C{^{1}H} spectra were obtained on a Varian As 400 MHz spectrometer with chemical shifts referenced to residual solvent $CDCl_3$. Elemental analyses were performed via CHNS-932 (LECO) in Tubitak Microlab and melting points were determined by electrothermal melting point detection apparatus.

The DTA and TG curves were obtained by using TG-DTA Perkin Elmer Diamond system apparatus. The measurements were performed under a dynamic nitrogen atmosphere at a flow rate of 200 mL min^{-1} up to 1000°C. The heating rate was 10°C min^{-1} and the samples changing in mass from 5 to 10 mg were contained in platinum crucible. All the experiments were performed twice for repeatability and the results show good reproducibility with the smaller variations in the kinetic parameters. α-Al_2O_3 was used as a reference material.

Results and discussion

The imidazolinium and benzimidazolium bromide salts with pentafluor substituents on N atom were synthesized. The imidazolinium and benzimidazolium salts are high melting colorless solids. They were obtained in good yields (**I**–**IV**) and characterized by elemental analysis and NMR spectroscopy. ^{1}H NMR spectra is a useful spectroscopic probe for structure elucidation of diazol(in)ium salts. Thus, (NCHN) resonances in **I**–**IV** are found at 9.59–11.71 ppm (Table 1). These downfield chemical shifts are characteristic for diazol(in)ium salts.

The salts are soluble in ethanol, acetone, chloroform, methanol, methylenechloride. Analytical and physical data of the salts are shown in Table 2.

Table 1 Analytical and physical data of salts **I**–**IV**

Compounds	Color	Yield/%	m.p./%	Carbon/%		Nitrogen/%		Hydrogen/%	
				found	calc.	found	calc.	found	calc.
I	white	92	236	51.64	51.95	6.31	6.06	5.00	4.33
II	white	92	199	55.96	56.36	5.52	5.48	3.74	3.91
III	white	91	145	53.53	53.73	5.89	5.97	2.94	2.99
IV	white	92	191	44.87	45.08	5.12	5.01	1.40	1.61

Table 2 ^{1}H and ^{13}C NMR data of salts **I**–**IV**

Compound	^{1}HNMR		^{13}CNMR	
	Chemical shift, δ/ppm	Assignment	Chemical shift, δ/ppm	Assignment
I	9.59	[s, 1H, CH]	158.42	[CH]
	3.88	[q, 4H, *J*=4.4 Hz, NCH_2CH_2N]	40.25	[NCH_2CH_2N]
	5.11	[s, 2H, $CH_2C_6F_5$]	48.57	[$CH_2C_6F_5$]
	4.90	[s, 2H, 2,4,6-$CH_2C_6H_2(CH_3)_3$]	46.81	[2,4,6-$CH_2C_6H_2(CH_3)_3$]
	2.36	[s, 6H, 2,4,6-$CH_2C_6H_2(CH_3)_3$]	21.12	[2,4,6-$CH_2C_6H_2(CH_3)_3$]
	2.26	[s, 3H, 2,4,6-$CH_2C_6H_2(CH_3)_3$]	20.30	[2,4,6-$CH_2C_6H_2(CH_3)_3$]
	6.89	[s, 2H, 2,4,6-$CH_2C_6H_2(CH_3)_3$]	107.07, 125.15, 130.08, 136.68, 138.16, 139.48, 144.52, 147.02	[Ar-C]
II	10.87	[s, 1H, CH].	143.91	[CH]
	6.22	[s, 2H, $CH_2C_6F_5$]	47.82	[$CH_2C_6F_5$]
	5.82	[s, 2H, 2,4,6-$CH_2C_6H_2(CH_3)_3$]	39.97	[2,4,6-$CH_2C_6H_2(CH_3)_3$]
	2.29	[s, 6H, 2,4,6-$CH_2C_6H_2(CH_3)_3$]	21.28	[2,4,6-$CH_2C_6H_2(CH_3)_3$]
	2.27	[s, 3H, 2,4,6-$CH_2C_6H_2(CH_3)_3$]	20.37	[2,4,6-$CH_2C_6H_2(CH_3)_3$]
	6.91	[s, 2H, 2,4,6-$CH_2C_6H_2(CH_3)_3$]	96.33, 112.72, 114.39, 124.66, 127.66, 127.80, 130.45, 131.31, 131.58, 138.29, 140.17	[Ar-C]
	7.44	[dd, 2H, *J*=8.0 Hz, Ar-H]		
	7.50	[dt, 2H, *J*=7.6 Hz, Ar-H]		
III	11.71	[s, 1H, CH]	147.08	[CH]
	6.19	[s, 2H, $CH_2C_6F_5$]	52.01	[$CH_2C_6F_5$]
	5.89	[s, 2H, $CH_2C_6H_5$]	39.58	[$CH_2C_6H_5$]
	7.34–7.63	[m, 9H, Ar-H]	107.01, 112.75, 114.58, 127.86, 128.56, 129.48, 131.25, 132.63, 136.85, 139.31, 141.30, 143.74, 144.51	[Ar-C]
IV	11.41	[s, 1H, CH]	147.15	[C-H]
	6.24	[s, 4H, $CH_2C_6F_5$]	39.46	[$CH_2C_6F_5$]
	7.67	[m, 4H, Ar-H]	106.88, 113.27, 128.36, 130.95, 136.93, 139.43, 144.71	[Ar-C]

Thermal stability

The imidazolinium and benzimidazolium bromide salts with pentafluorobenzyl substituthent(s) on N atom(s) (**I**, **II**, **III** and **IV**) were studied by thermogravimetric analysis from ambient temperature to 1000°C in nitrogen atmosphere. Typical TG, DTG and DTA curves for compound are shown in Figs 1, 2 and 3 and the initial and final temperatures and total mass losses for each step in the thermal decomposition of complexes are given in Table 3, together with temperatures of greatest rate of decomposition (DTG_{max}), evolved moiety and the theoretical percentage mass losses. The decomposition of all the compounds was very similar in character and occurs in one-stage. Compounds **I**, **II**, **III** and **IV** are thermal stable up to 205, 170, 185 and 166°C, respectively.

It was found that pyrolytic decomposition occurs together with the melting except compound **III**. Compound **III** exhibits decomposition following melting.

The thermal decomposition pattern of LR_1, LR_2, LR_3 where *L*=benzimidazolium salt and *R*=CH_2–Mes, CH_2–Mes, CH_2–C_6F_5 shows a different decomposition pattern due to the different *R* groups attached to the organotin moiety.

From the TG curve for compound **I**, it appears that the sample decomposes in one stage over the temperature range 205–302°C with a mass loss 74.4% in mass. The decomposition process of compound **II** is similar to compound **I**. The stability of compound **II** is less than that of compound **I** as it decomposes at 170°C. From the corresponding DTA profiles, only one exothermic peak for both **I** and **II** is noted. The

Table 3 TG, DTG and DTA data for the imidazolinium and benzimidazolium bromide salts

Salt	Step	DTA peak maximum/°C	DTG_{max}/°C	Temperature range/°C	DTA	Residue mass %
I	I	232	274	205–302	exo	25.6
	residue	>302				
II	I	187	215	170–243	exo	20.0
	residue	>243				
III	I	139, 195	226	185–243	endo, exo	18.7
	residue	>243				
IV	I	182	218	166–239	exo	26.25
	residue	>239				

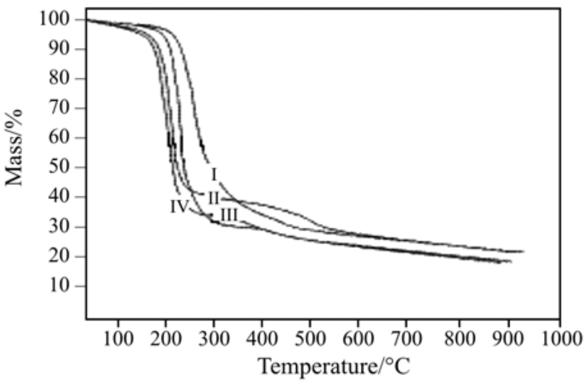

Fig. 1 Typical TG curves for compounds (**I**, **II**, **III**, **IV**)

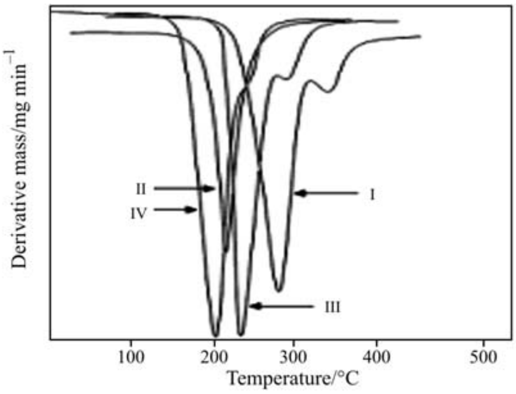

Fig. 2 Typical DTG curves for compounds (**I**, **II**, **III**, **IV**)

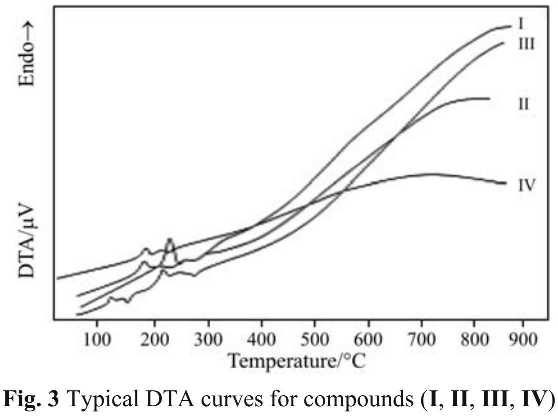

Fig. 3 Typical DTA curves for compounds (**I**, **II**, **III**, **IV**)

maxima of these peaks which are due to the melting of **I** and **II** are found to be 232 and 187°C, respectively.

Compound **III** exhibited a one step decomposition process. This stage occurs at the temperature range of 185–243°C with an 81.3% mass loss. The DTA profile shows one exothermic and one endothermic peak at 139 and 195°C, respectively. The first peak corresponds to the melting while the second one does to the decomposition of **III**. Compound **IV** is thermally stable up to 166°C and shows a one step decomposition process in the temperature range 185–243°C accompanied with an 81.3% mass loss. Among these three compounds (**II**, **III**, **IV**) having the similar decomposition steps, the more stably of **III**, as compared to **II** and **IV**. The thermal stabilities of all compounds (**I**, **II**, **III** and **IV**) were found as **I**>**III**>**II**>**IV**. The structure is stretched by substitutive of the pentafluor group and then the stability of compound **IV** decreases. However, the fact that **III** is more stable than **II** is unexpected. The stability of compound **II** decreases compare to **III** due to sterical stretch, whilst CH_2–Mes substituted is expected to increase it. For the same reason both **I** and **II** are more stable than **III**.

Thermal decomposition

The kinetics of heterogeneous condensed phase reactions that occur in non-isothermal conditions is usually described by the equation,

$$\beta\frac{\mathrm{d}\alpha}{\mathrm{d}T}=Af(\alpha)\exp\left(\frac{-E}{RT}\right) \qquad (1)$$

where α is the degree of conversion, β is the linear heating rate, and *A* is pre-exponential factor, and $f(\alpha)$ is the differential conversion function. In order to calculate the kinetic parameters, different reaction models may be used. The fraction of mass loss, α and corresponding $(1–\alpha)^n$ are calculated from TG curves, where *n* depends upon the reaction model. In studying the decomposition kinetics, three of the methods given in the literature were chosen: Coats–Redfern (CR), van Krevelen (vK), MacCallum–Tanner (MC) which can be expressed by following equations:

- The Coats–Redfern method

$$\ln\left[\frac{g(\alpha)}{T^2}\right]=\ln\left[\frac{AR}{\beta E}\left(1-\frac{2RT}{E}\right)\right]-\left(\frac{E}{RT}\right) \quad (2)$$

- The van Krevelen method

$$\ln g(\alpha)=\ln\left[\frac{A(0.368/T_\mathrm{m})^{\frac{E_\mathrm{a}}{RT_\mathrm{m}}}}{\beta\left(\frac{E_\mathrm{a}}{RT_\mathrm{m}}+1\right)}\right]+\left(\frac{E_\mathrm{a}}{RT_\mathrm{m}}+1\right)\ln T \quad (3)$$

- The MacCallum–Tanner method

$$\log g(\alpha)=\log\left(\frac{AE}{\beta R}\right)-0.4828E^{0.4351}-\left(\frac{0.449+0.217E}{10^{-3}T}\right) \quad (4)$$

In the equations above, $g(\alpha)$, T_m, E, R, are the integral function of conversion, DTG peak temperature, activation energy (kJ mol^{-1}), and gas constant (8.314 J mol^{-1} K^{-1}), respectively. The kinetic parameters were calculated from the linear plots of the left-hand side of kinetic equations (Eqs (2) and (4)) *vs.* $1/T$. For van Krevelen equation (Eq. (3)) the left-hand side is plotted *vs.* $\ln T$. The values E and A were calculated from the slope and intercept of the straight lines, respectively. According to Coats and Redfern method, the plot of ln ($g(\alpha)/T^2$) *vs.* $1/T$ gives straight line with slope equals to $-E/R$. The activation energies of complexes were calculated from Fig. 4 and given in Table 4.

Figure 5 shows how to determine the activation energy by the method of van Krevelen from the mass loss in the curves taken under nitrogen atmosphere with heating rate of 10°C min^{-1}. The activation energies can be calculated from the slopes of the $\log g(\alpha)$ *vs.* $\ln T$ plots.

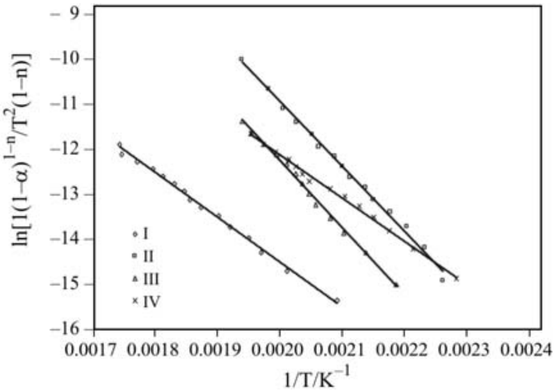

Fig. 4 Coats–Redfern plots of imidazolinium and benzimidazolium salts

The MacCallum–Tanner method also provides an approximated form of the rate of degradation as a function of temperature. Thus, the rate of degradation can be expressed by Eq. (4). Figure 6 represents a plot of $\log g(\alpha)$ *vs.* $1/T$ obtained using this approximation. From the plots it is possible calculate the activation energies from the slopes. Those of the imidazolinium and benzimidazolium salts were found to be 83.6 to 124.9 kJ mol^{-1}.

For all of the methods, it is possible to determination of the pre-exponential factor and reaction order is possible from the expression of $g(\alpha)$ in Eq. (3) where $n\neq1$:

$$g(\alpha)=\frac{1-(1-\alpha)^{1-\mathrm{n}}}{1-n}$$

The linearization curves of the imidazolinium and benzimidazolium salts obtained using the methods mentioned above and presented in Figs 4–6. Moreover, Table 4 summarizes the reaction orders, pre-exponential factors, correlation coefficients and the activation energies obtained by the three different methods examined in this study. The results are in good agreement with the values obtained from all of them. They indicate that the values of all methods are comparable. As seen in Table 4, the value of correlation coefficients of linearization curves of imidazolinium

Table 4 Kinetic data on imidazolinium and benzimidazolium salts

Method	Complexes	n	E/kJ mol^{-1}	ln$A$/s^{-1}	Correlation coefficient, r	$\Delta S^\#$/J mol^{-1} K^{-1}	$\Delta H^\#$/kJ mol^{-1}	$\Delta G^\#$/kJ mol^{-1}
CR	**I**	1.9	82.90	16.58	0.99814	–112.0	78.30	139.6
	II	1.9	119.4	28.54	0.99764	–11.60	115.3	121.0
	III	1.7	124.6	28.85	0.99809	–9.200	120.4	125.0
	IV		80.10	20.26	0.99774	–80.60	76.00	115.6
vK	**I**	2.3	97.80	23.12	0.99849	–57.70	93.20	124.8
	II	2.1	135.2	40.84	0.99789	90.60	131.1	86.90
	III	1.9	138.5	38.23	0.99839	68.70	134.3	100.0
	IV	1.0	89.90	25.66	0.99789	–35.60	85.80	103.3
MC	**I**	1.9	83.60	25.16	0.99849	–40.70	79.00	101.3
	II	1.9	119.4	36.87	0.99789	57.50	115.3	87.20
	III	1.7	124.9	37.17	0.99834	59.90	120.7	90.80
	IV	0.9	80.00	26.28	0.99814	–30.50	75.90	90.90

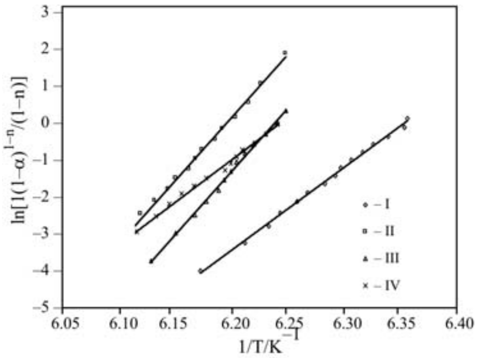

Fig. 5 Van Krevelen plots of imidazolinium and benzimidazolium salts

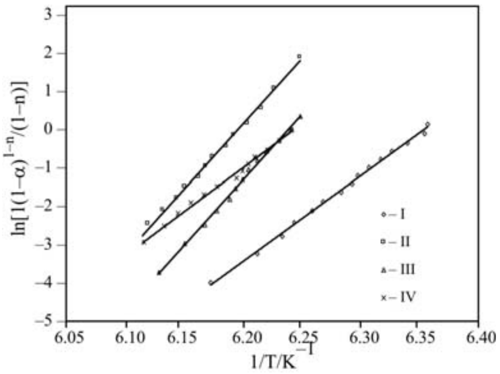

Fig. 6 MacCallum–Tanner plots of imidazolinium and benzimidazolium salts

and benzimidazolium salts are approximately 1.00. The kinetic data obtained by different methods agree with each other.

The enthalpy $\Delta H^{\#}$, activation entropy $\Delta S^{\#}$, and the free energy of activation $\Delta G^{\#}$, of imidazolinium and benzimidazolium salts were calculated using the following relations [24]:

$$\Delta S^{\#} = 2.303\log\left(\frac{Ah}{kT}\right)R$$

$$\Delta H = E - RT$$

$$\Delta G^{\#} = \Delta H - T\Delta S^{\#}$$

where *h* is the Planck constant and *T* is the temperature at the maximum rate of mass loss, *A* is the pre-exponential factor. The thermodynamic parameters calculated were reported in Table 4.

Conclusions

A study on the thermal decomposition of the imidazolinium and benzimidazolium salts was carried out by using three kinetic methods. The decomposition kinetics was investigated by evaluating the dynamic thermogravimetric data obtained at a single heating rate. The thermal decomposition of the complexes took place in one step in exothermic reaction up to 327°C. The activation energy *E*, the entropy change $\Delta S^{\#}$, enthalpy change $\Delta H^{\#}$ and Gibbs free energy change $\Delta G^{\#}$, were calculated by thermogravimetry analysis (TG) and the melting points by differential thermal analysis (DTA) and melting point apparatus. It was found that the thermal stabilities and activation energies of all compound (**I**, **II**, **III** and **IV**) follow the order **I**>**III**>**II**>**IV**, $E_{\mathrm{IV}}<E_{\mathrm{I}}<E_{\mathrm{II}}<E_{\mathrm{III}}$, respectively.

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