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ORIGINAL PAPER

Comparative thermal stability studies of some isomeric phenolic β-diketones and their phenolic pyrazoles by thermogravimetric analysis

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ABSTRACT The thermal degradation and thermal stability of some isomeric phenolic β-diketones I(a-b) their phenolic pyrazoles II(a-b) and III(a-b) were studied with thermogravimetric analysis TGA. The isomeric phenolic β-diketones I(a-b) were synthesized via modified Baker-Venkataraman rearrangement. Isomeric β-diketones were converted to their phenolic pyrazoles II(a-b) and III(a-b) on reaction with phenyl hydrazine. Factors effecting thermal stability based on the initial decomposition temperature (IDT), temperature of maximum weight loss (T_{max}), decomposition temperature ranges and activation energy (E_a) of the decomposition reaction were studied. Activation energy, enthalpy and entropy of all the synthesized products were calculated by Horowitz and Metzger's method, an integral method for the determination of reaction order from the thermogravimetric data. On the basis of IDT, ortho isomer of phenolic β-diketones (Ib) was found to be more stable than that of its para counterpart (Ia). Among the phenolic pyrazoles, compound IIIa exhibited the highest initial decomposition temperature (IDT) followed by IIb, IIa and IIIb (in decreasing order).

Keywords: Activation energy, Phenolic β-diketones, Phenolic pyrazole, Thermogravimetric analysis, Thermal stability

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INTRODUCTION

Phenolic β-diketones have drawn a lot of interest due to their importance as good ligands for chelation with metals (Vigato et al., 2009; Sheikh et al., 2013) and as starting materials for the preparation of biologically active pyrazoles (Pradhan & Goyal, 2015) benzothiazepines (Ahmad et al., 2000) and benzodiazepines (Heravi et al., 2008). Pyrazoles are known for their potential biological activity (Balbi et al., 2011; Schmidt & Dreger, 2011) and complexation with transition metals (Bieller et al., 2006; Jaćimović et al., 2009). Traditional and new synthetic methods are being used to prepare new materials for medicine, agriculture and other studies. Usually, most unsymmetrical pyrazoles are targeted, prepared and reported (Wang et al., 2000; Heller & Natarajan, 2006; Fustero et al., 2011; Schmitt et al., 2015). Phenolic pyrazoles have been synthesized by cyclocondensation of phenolic β-diketones with hydrazine derivatives (Nasseri et al., 2014; Nascimento et al., 2015).

The synthesis of pyrazoles from phenolic β-dicarbonyl compounds and hydrazine derivatives is by far the most widely used method. With unsymmetrical diketones, isomeric pyrazole can theoretically be produced and sometimes, both can be isolated from the reaction mixture (Nishiguchi et al., 2002). Many structural and experimental factors are involved in selective formation of one of the two isomeric compounds. Several attempts have been made to devise methods for the selective synthesis of one of the two possible isomeric pyrazoles through the use of a functional derivative of β-dicarbonyl compound.

In this article, different isomeric phenolic β-diketones I(a-b), and their pyrazole derivatives II(a-b) and III(a-b) were prepared according to the reported procedures (Ahmad et al., 1990; Ahmad et al., 1996; Ahmad et al., 1997) and their comparative thermal properties were examined by TGA. Thermal stabilities based on initial decomposition temperature (IDT), temperature of maximum weight loss (T_{max}), decomposition temperature range, activation energy (E_a), enthalpy, entropy and order of the

decomposition reaction were studied. The Horowitz–Metzger (HM) (Horowitz & Metzger, 1963) approximation method was employed for the determination of thermodynamic and kinetic parameters.

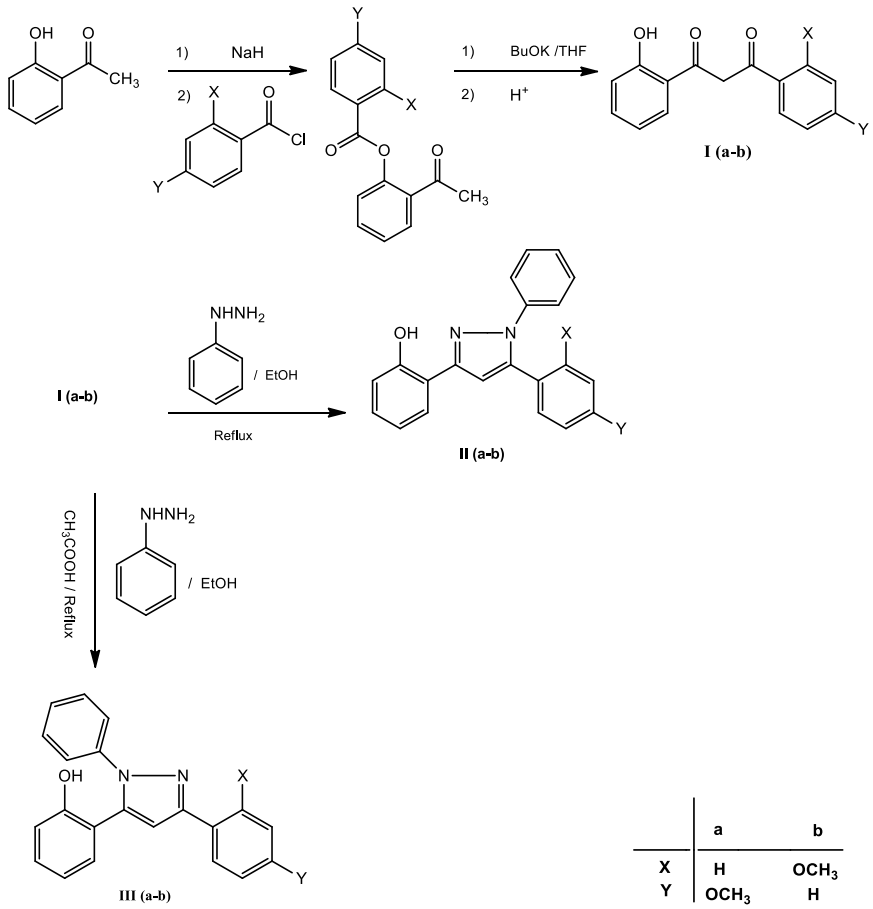
MATERIALS AND METHODS

Isomeric phenolic β-diketones 1-(2′-hydroxyphenyl)-3-(4″-methoxyphenyl)-1,3-propanedione (Ia) and 1-(2′-hydroxyphenyl)-3-(2″-methoxyphenyl)-1,3-propanedione (Ib) were synthesized via modified Baker-Venkataraman rearrangement (scheme 1). The ^{1}H-NMR, ^{13}C-NMR and MS data for the compounds were previously published (Ahmad et al., 1990; Ahmad et al., 1997). Purification was performed by column chromatography using ethyl acetate as eluent. Yellow crystals of Ia (yield 89%, m.p. 125°C) and Ib (yield 63%, m.p. 79°C) were obtained by slow evaporation of their respective ethanolic solutions.

Isomeric β-diketones were subjected to cyclocondensation reaction with phenyl hydrazine in ethanol to get their respective pyrazole derivatives II(a-b) and III(a-b) (Scheme 1). Cyclocondensation led to the formation of regioisomers, 1-Phenyl-3-(2′-hydroxyphenyl)-5-(4″-methoxyphenyl)-pyrazole (IIa) (yield 65%, m.p. 133°C), 1-Phenyl-3-(2′-hydroxyphenyl)-5-(2″-methoxyphenyl)-pyrazole (IIb) (yield 47%, m.p. 120°C), and 1-Phenyl-3-(4″-methoxyphenyl)-5-(2′-hydroxyphenyl)-pyrazole (IIIa) (yield 43.2%, m.p. 186°C), 1-Phenyl-3-(2″-methoxyphenyl)-5-(2′-hydroxyphenyl)- pyrazole (IIIb) (yield 35 %, m.p. 140°C) in neutral and acidic medium, respectively. The ^{1}H, ^{13}C-NMR and MS data for the pyrazole derivatives was formerly reported by Ahmad and Zia ul Haq in 1996 (Ahmad et al., 1996). All the synthesized compounds were purified by column chromatography on silica gel using ethyl acetate as eluent.

Instruments

Thermogravimetric analysis was performed with a thermal analysis TGA thermogravimetric analyzer TGA-7 by Perkin-Elmer under argon. Heating scan carried out with heating rate of 10°C/min. Isothermal scan at 220 and 300°C for 180 minutes was performed.



Scheme 1 Synthesis of isomeric phenolic β-diketones I(a-b), their phenolic pyrazoles II(a-b) and III(a-b)

RESULTS AND DISCUSSION

TGA analysis and thermal stability

The thermal properties of synthesized compounds were evaluated by TGA. Fig. 1 shows the thermo analyses of Ia and Ib in Argon. Compound Ib started to degrade around 230°C and lost 100% weight around 355 °C leaving no residue. During this single stage decomposition, three moles of CO_2 one mole of acetylene (HC ≡ CH), one mole of H_2O and two moles of benzene evolved. The para isomer (Ia) began to lose weight around 196°C (Fig. 1) in one-step pyrolysis. The process came to an end around 350 °C with an overall weight loss of 96%. The residue was confirmed as char. The products of disintegration were identified as two moles of CO_2 one mole of methane (CH_4), one mole of oxygen (O_2) and two moles of benzene. On the basis of IDT, ortho isomer (Ib) was more stable than its para counterpart (Ia).

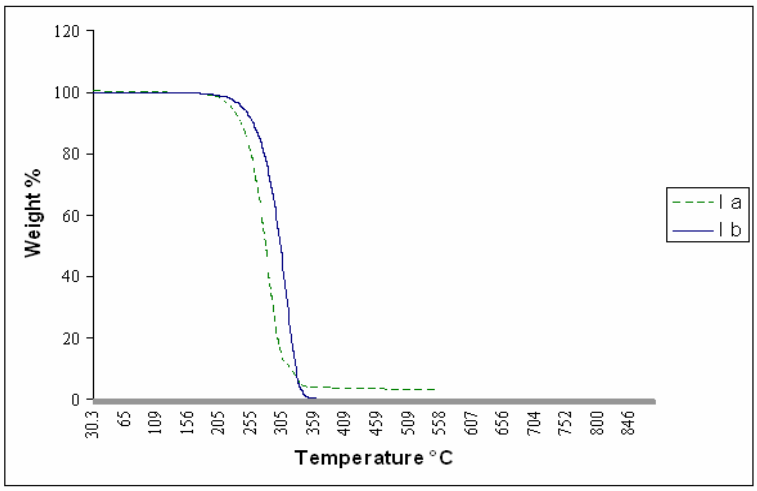


Fig. 1 TGA Thermogram of compounds Ia and Ib in Argon

On the other hand, para isomer due to its resonance stability melted at higher temperature and also left residue. The isothermal (220 °C) heating of the two isomers, Ia, and Ib (Fig. 2) supported the results of TGA. Despite sharing the identical time interval (9 minutes) for commencement of weight loss, the remaining part of TGA curve clearly indicates the stability pattern of the isomers for fifty % mass – loss, 1b took 68 minutes as compared to Ia which achieved this weight – loss in just 55 minutes. At the completion of this experiment (173 minutes) the residue (char) for Ib was 4% higher than that for 1a.

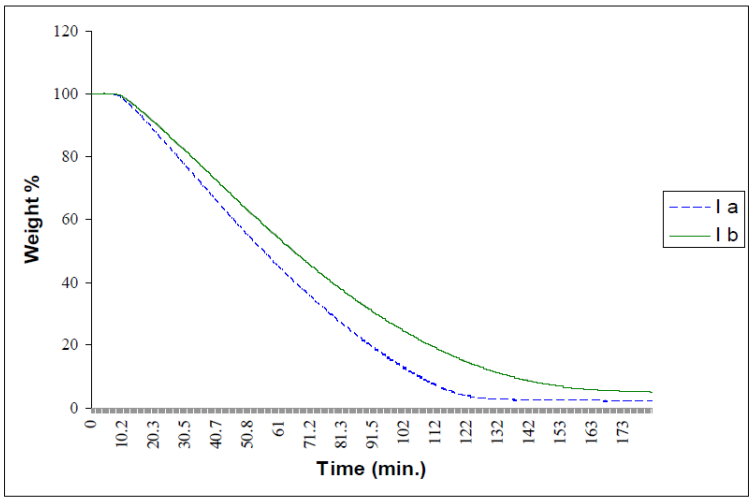


Fig. 2 Isothermal TGA Thermogram of compounds Ia and Ib at 220 °C in Argon

The second isothermal (300 °C, Fig. 3) test provided more evidence for the stability of Ib over Ia. Since the energy content at this temperature was appreciably higher than that at 220 °C, so almost 100% weight loss was achieved within 22 minutes by both isomers. It took 18 minutes for Ia to pyrolyze

completely whereas Ib took 22 minutes. Overall weight loss was very sharp in this instance. Fifty percent weight loss required 15 and 18 minutes for Ia and Ib, respectively. Though same intermolecular and intramolecular forces of attraction were applicable but the higher content of energy corresponding to this temperature prevailed over them in a relatively short time.

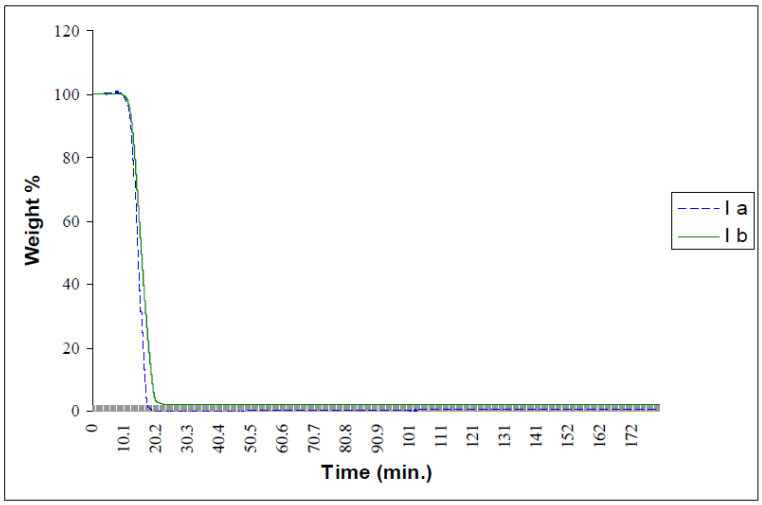


Fig. 3 Isothermal TGA Thermogram of compounds Ia and Ib at 300 °C in Argon

Fig. 4 presents TG curves for IIa, IIb, IIIa and IIIb. All four compounds showed single stage degradation with sharp weight loss, i.e., within a small range of temperature, stable residues were obtained. Compound IIIa exhibited the highest initial decomposition temperature (IDT) followed by IIb, IIa and IIIb (in decreasing order). This stability may be due to intramolecular hydrogen bonding and resonance in (IIIa). The temperatures of fifty percent weight loss for IIa, IIb, IIIa & IIIb were 320, 340, 365, and 313°C respectively. At the completion of pyrolysis, IIIb showed highest percentage of residue followed by IIa, IIb, and IIIa (Table 1).

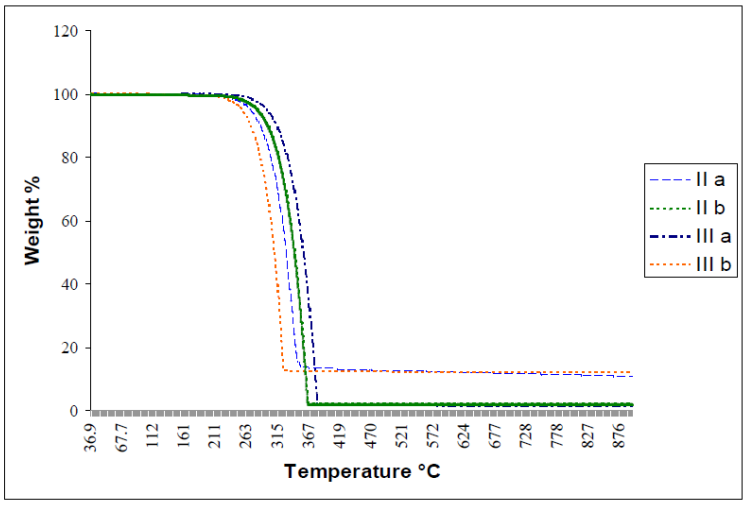


Fig. 4 TGA Thermogram of compounds IIa, IIb, IIIa and IIIb in Argon

Char was formed as residue in all cases. More char in cases of IIIb and IIa indicates the development of conjugation and evolution of small molecules like hydrogen towards the termination of degradation. All the isomers gave similar degradation product i.e, benzene, nitrogen, methane, acetylene, hydrogen, carbon monoxide, water, etc. More hydrogen and water was evolved from IIIb and IIa in comparison with the other isomers. This observation supported the production of higher amount of residue in these two instances. On the basis of activation energies (Table 2) IIIa was found to be the most stable isomer.

Fig. 5 gives the isothermal TGA traces for the isomers at 300°C. As the temperature was raised to 300°C the energy level goes up considerably and the complete pyrolysis of isomers (IIa, IIb, IIIa, and IIIb) was obtained in less than 65 minutes (Fig. 5). It took 60 minutes for IIIa to give stable residue (~2%), 47 minutes for IIb to leave 0.5% residue, 30 minutes for IIa to render 8% residue and 19 minutes for IIIb to yield 12% residue. For IIa and IIIb, the weight loss curve was very sharp as compared to IIb and IIIa, higher amounts of small volatile molecules were expected from the former ones and the results corroborate this assumption.

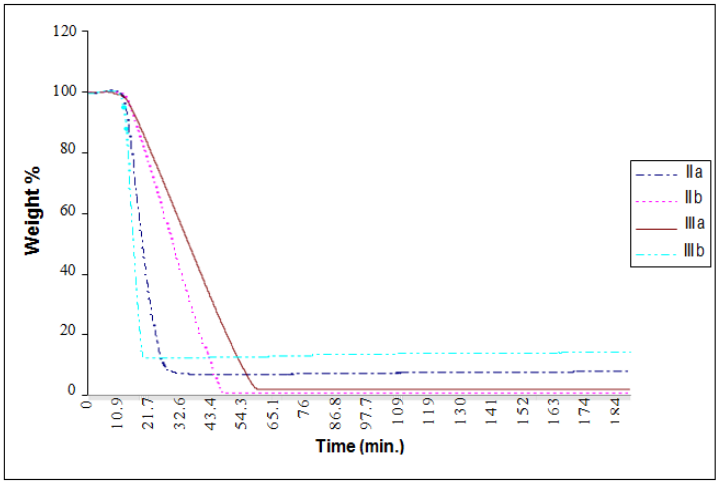


Fig. 5 Isothermal TGA Thermogram of compounds IIa, IIb, IIIa and IIIb at 300 °C in Argon

Kinetic and thermodynamic parameters

The thermal behavior and properties of various types of materials have been reliably studied by thermogravimetric analysis (TGA) over many decades (Singh et al., 2012; Shahbazi et al., 2017). For the analysis of drugs and substances of pharmaceutical interest thermal analysis serves as a routine method (Araújo et al, 2005). The chemical steps of the investigated degradation and the evaluation of the kinetic parameters for each step can be determined by these methods.

Numerous equations have been put forward for analyzing TG curves and obtaining kinetic parameters from them (Mallakpour et al., 2009). From these, Horowitz and Metzger was applied, that is an integral method for the calculation of activation energies and reaction order from the thermogravimetric data (Mallikarjun, 2004).

Horowitz and Metzger method

The Horowitz–Metzger equation can be expressed as follow

$$lnln(1-C)=E_a\,\theta/RT^2_{max} \quad (1)$$

$$Where\ 1-C = W_i-W_f/W_t-W_f$$

$$And\ \theta= T-T_{max}$$

T_{max} is the reference temperature showing maximum weight loss, W_t is the mass remaining at a given temperature, W_i and W_f are the initial and final masses, respectively, and E_a is the activation energy of pyrolysis.

In this method, double logarithm of the reciprocal of weight fraction of the reactant was plotted versus temperature difference θ, and the activation energy was calculated from the slope of the straight line.

Kinetic parameters such as entropies ΔS, Gibbs free energy ΔG, enthalpy ΔH were calculated using the following equations (Yousef et al., 2013).

$$\Delta H = E-RT_{max} \quad (2)$$

$$\Delta G = \Delta H - T_{max}\,\Delta S \quad (3)$$

$$\Delta S= 2.303[\log(Ah/kT_{max})]R \quad (4)$$

Where k, h and A were the Boltzman, Planck and Arrhenius constants, respectively.

The calculated values of E_a, ΔS, ΔH are given in Table 2. The activation energies were found in the range 22969-98205 (J/mole). The thermal stability of the compounds was reflected by their high values of activation energies. Clear difference was observed in thermal decomposition and thermal stability of the synthesized compounds. Significant variation in the thermal stabilities of the compounds was due to the differences in their structures. The positive enthalpy values for I(a-b), II(a-b) and III(a-b) indicate that decompositions were endothermic. The decompositions increased with the raise of temperature. The negative value of the entropy for Ia, IIa, IIIb indicates that undecomposed fragments were less ordered than activated fragments. The decomposition reaction for Ia, IIa, IIIb proceded at a lower rate than for Ib, IIb and IIIa.

Table 1 Thermal stability data from TGA curves

Sample	IDT °C	10% weight loss	Residual weight (%)				
		°C	300 °C	350 °C	400 °C	500 °C	700°C
I a	196	240	19	4	4	4	4
I b	230	260	45	2	0	0	0
II a	258	282	83	14	13	12	11
II b	260	289	88	34	3	3	2
III a	283	318	94	58	2	2	2
III b	231	268	61	12	12	12	12

Table 2 Activation energies, enthalpy, entropy and order of reaction of the degradation reaction of compounds I(a-b), II(a-b) and III (a-b)

Compound	E_a (J/mole)	Enthalpy (J/mole)	Entropy (J/mole K)	Order of reaction
I a	22969.82	20687.63	-96.33	3
I b	52762.91	50317.76	138.67	3
II a	28503.78	25877.39	-79.9	4
II b	70845.84	68135.48	228.86	5
III a	98205.72	95413.05	406.14	6
III b	26299.68	23806.31	-86.18	3

CONCLUSION

Isomeric phenolic β-diketones and their phenolic pyrazoles were synthesized using standard protocols. The thermal behaviour of compounds was studied by TGA. The thermogravimetric data enabled to establish information on the thermal stability of the compounds. On the basis of IDT, ortho isomer (Ib) of phenolic β-diketones was found to be more stable than its para counterpart (Ia). For phenolic pyrazoles following order of stability was observed.

IIIa > IIb> IIa> IIIb

The stability order is in reasonably good agreement with the values of activation energies obtained. In the early part of pyrolysis, intramolecular hydrogen bonding and resonance play dominant role. However in the later part, development of conjugation and expulsion of smaller volatile products assume importance. Except Ib, all other compounds gave char as stable residue. Isothermal experiments confirm the results of dynamic TGA studies.

Author Contribution Statement Both the authors contributed equally to this work.

Conflict Of Interest The authors declare that they have no conflict of interest.

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