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Research Article

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Thermal studies of some biologically active new aryl esters of 1,1'-bis(4-hydroxyphenyl)cyclohexane

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ABSTRACT

Thermal study of some biologically active aryl esters of bisphenol-C derivatives have been investigated using TG and DSC techniques under nitrogen atmosphere at the heating rate of 10ºC min^{-1}. The nature and position of the substituents affected DSC transitions, thermal stability and kinetic parameters. DSC curves of all compounds showed endothermic transitions in the range 120-257^{0}C and corresponding enthalpy change (ΔH) in the range 18-58 kJmol^{-1}. Aryl esters are thermally stable up to about 215-375^{0}C and followed either a single or two steps degradation kinetics due to structural dissimilarity. They followed either fractional or integral order degradation kinetics. Different magnitudes of n, E_a and A suggested different degradation mechanisms. A large and negative magnitudes of ΔS^* confirmed highly ordered transition states, while a large and positive magnitudes of ΔS^* confirmed less ordered transition states.

Keywords: Kinetic parameters, aryl esters, thermal stability, kinetic parameters

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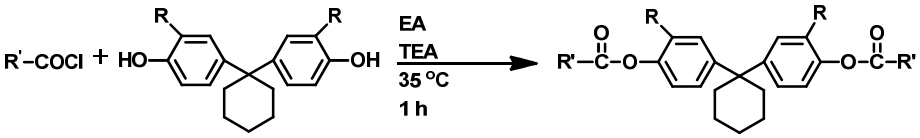
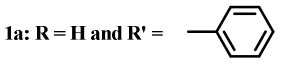
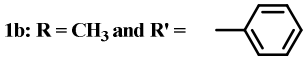
INTRODUCTION

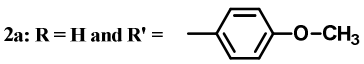
Aryl esters are commonly found in a varietyof biologically active and natural compounds [1-5].Suitably substituted aryl esters of aromatic acids provide a convenient source of fairly readily prepared nematogenic compounds [6]. Thermal analysis is used as a quick and reliable technique for studying crystallinity, purity, thermal stability, polymorphism, and glass transition evaluation [7-11]. Before final testing of the potentially bioactive compounds thermal analysis is very important. Thermodynamic and kinetic study of solid-state reactions is a challenging and difficult task because of complexity resulting from the great variety of factors with diverse effects such as reconstruction of solid-state crystal lattice, formation and growth of new crystallization nuclei, diffusion of gaseous reagents or reaction products, etc [12,13]. Thermal analysis of the materials provides reliable information on the physico-chemical parameters characterizing the processes of isothermal and non-isothermal decomposition [14]. Kinetic parameters such as activation energy, pre-exponential factor and reaction order provide insight of degradation mechanism [15,16].

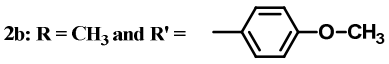
To the best of our knowledge no work has been reported on thermal analysis of biologically active arylesters of bisphenol-C derivatives, which prompted us to take up present investigation. In present work we have reported the effect of substituent on thermal behaviour of aryl esters of bisphenol-C (Scheme I). In this paper, we have reported the effect of substituents on the thermal behaviour of aryl esters of bisphenol-C.

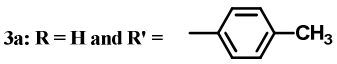


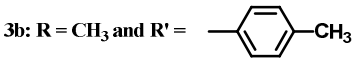


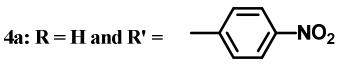


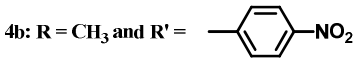


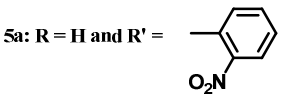


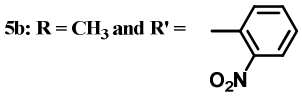


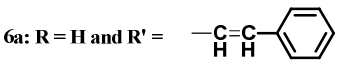


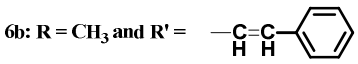












Scheme I Synthesis of bisphenol-C derivetives

EXPERIMENTAL SECTION

Materials

Biologically active aryl esters of bisphenol-C were synthesized according to our recent work [17].

Measurements

Differential scanning calorimetric (DSC) measurements were carried out on a Shimadzu DSC60 at the heating rate of $10^oC\ min^{-1}$in nitrogen atmosphere with flow rate 50 mL min^{-1}. About 2-3 mg of the sample was accurately weighed in an aluminium crucible and sealed using a crimper, and immediately subjected to a temperature scan from 25 to 300 ^0C with an empty aluminium crucible as the reference. Thermogravimetric (TG) measurements were carried out on a Shimadzu DTG-60H at the heating rate of $10^oC\ min^{-1}$in nitrogen atmosphere with flow rate 50 mL min^{-1}. About 3-6 mg sample was weighed accurately in an open alumina pan and subjected to a temperature scan from room temperature to 800^0C.

RESULTS AND DISCUSSION

DSC thermograms of **1a-6a**and **1b-6b**at 10^oCmin^{-1} heating rate under nitrogen atmosphere are presented in Figs. 1 and 2, respectively. The melting transitions (T_m), along with heat of fusion (ΔH) and entropy of transitions (ΔS) are listed in Table 1.From Table 1, it is observed that **1a-6a** showed considerably higher T_m than those of **1b-6b** but no systematic trends is observed for ΔH and ΔS due to different packing densities of aryl esters. Symmetric molecules

(1a-6a) showed higher T_m than those of asymmetric molecules **(1b-6b)**. Substituted phenyl rings caused considerable lowering in T_m except **4a** and **4b** due to different nature of substituents and their positions (o, m, p). Methoxy substituent showed slightly lower T_m than methyl substituent, which may be due to more flexibility of methoxy group. **4a** and **4b** showed higher T_m than **5a** and **5b** due to different position of nitro group. Considerably high T_m of **4a** and**4b** are due to high packing density as compared to other aryl esters. Similarly substituted olefinic group also caused lowering in T_m. Similar trends are also observed for $\Delta H$and ΔS values. Thus nature, size and position of the substituents affected T_m,ΔH and ΔS values.

TGA thermograms of **1a-6a** and**1b-6b** at 10 ^{0}C min^{-1} heating rate in nitrogen atmosphere are presented in Figs 3 and 4, respectively. It is observed that **1a, 3a, 5a, 6a, 1b, 4b,** and **6b**followed single step decomposition, while **2a, 4a, 2b, 3b** and **5b** followed two step decomposition reactions. The initial decomposition temperature (T_o), temperature of 10 % weight loss, temperature of maximum weight loss (T_{max}), decomposition range, the % weight loss involved and residue remained at 500^{o}C are reported in Table 2. **1a-6a** and **1b-6b** are thermally stable upto about 225-290 and 135-305 ^{o}C, respectively. Thermal stability and decomposition behaviour of aryl esters are affected by their structure, nature, size and position of the substituents.

Associated kinetic parameters such as energy of activation (E_a), frequency factor (A) and order of the reaction (n) for all the aryl esters were derived according to Anderson-Freeman method [18].

$$\Delta \ln \frac{\mathrm{d}w}{\mathrm{d}t} = n\Delta \ln W - \left(\frac{E_a}{RT}\right)\Delta\left(\frac{1}{T}\right) \quad (1)$$

$$A = \left(\frac{E_a \beta}{RT^2}\right) \mathrm{e}^{\frac{E_a}{RT}} \quad (2)$$

$$\Delta S^* = R \ln\left(\frac{Ah}{kT}\right) \quad (3)$$

Where dw/dt is the rate of decomposition, W is the active mass, β is the heating rate, R is the gas constant, h is the Planck's constant, T is temperature and k is the Boltzmann constant. The least square values of above mentioned parameters along with regression coefficients (R^2) are reported in Table 3. The entropy change ΔS^* was determined at corresponding T_{max}. It is observed from Table 3 that aryl esters followed either integral or fractional order degradation kinetics. **1a**apparently followed one half order (0.56), while **1b** followed apparently zero order (0.28) kinetics. Both **2a** and **2b** followed apparently first order (**2a**: 1.17 and 0.72; **2b**: 1.2). **3a** and **3b** followed fractional order (0.53 and 0.70) kinetics. Both **4a** and**4b** followed fractional order (**4a**: 0.71 and 0.49; **4b**: 0.74).**5a** apparently followed second order (2.36), while **5b** followed apparently first order (**5b**: 0.8 and 1.06). **6a** apparently followed second order (1.81), while **6b** apparently followed first order (1.20). Thus, different nature, size and positions of the substituents caused different order degradation kinetics. No systematic trends for n, E_a, A and $\Delta S^*$are observed due to above mentioned reasons. In accordance to theory, rigid is the structure higher are the kinetic parameters E_a and A. A large and negative magnitudes of ΔS^* suggested that transition state is more in orderly state than that of aryl ester, while a large and positive magnitudes of ΔS^*suggested that transition state is more in disorderly state [19,20]. Degradation of the compound is a complex process and involves a variety of relations such as cleavage, rearrangement, branching, cross-linking, etc. The side substituents and ester linkages are weak linkages in aryl esters so selective degradation starts from such weak points with the evolution of carbon dioxide and other hydrocarbon gases with formation of free radicals, which further undergo secondary reactions to form new compounds and degrade at elevated temperature. A considerable amount of residue left at 500 ^{0}C for **4a** (47.8%), **5a** (37.5%),**6a** (15.4%), **3b** (11.4%), **5b** (44.6%) and **6b** (16.8%) suggested formation of highly thermally stable compounds. Other compounds practically decomposed into low molecular mass hydrocarbons. Thus, different molecular structures of aryl esters with different nature showed different thermal behaviour and degradation kinetics.

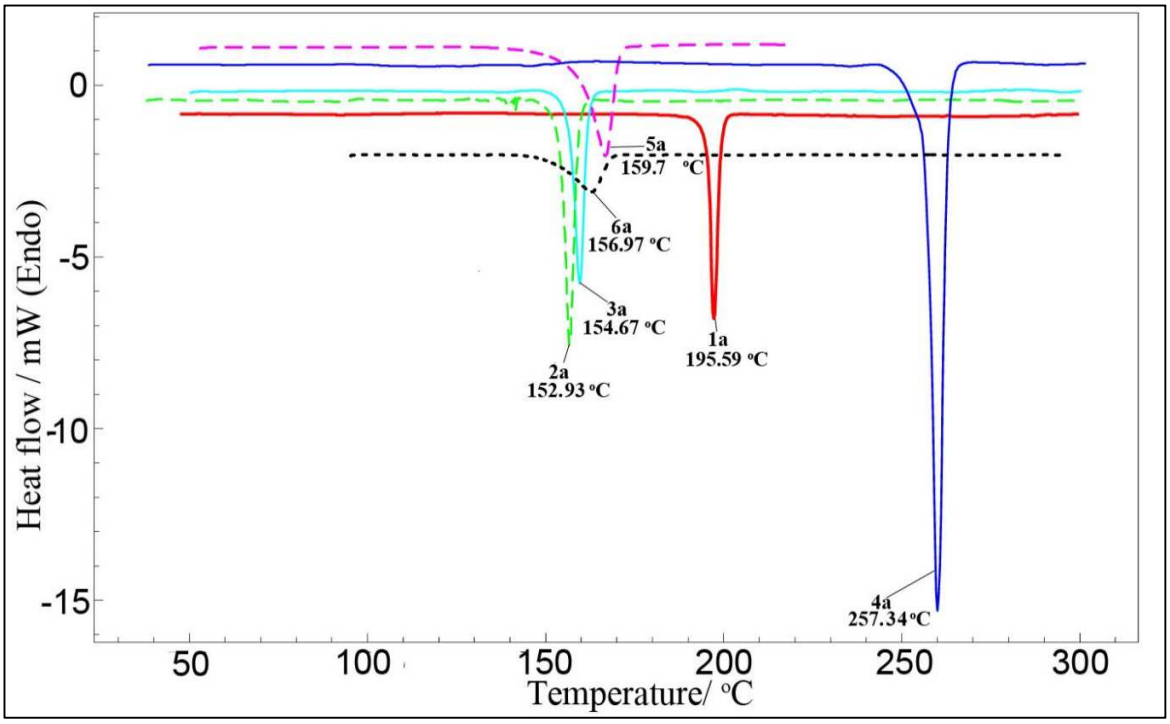


Fig. 1 DSC curves of aryl esters 1a-6a at 10 ^{0}C heating rate in nitrogen atmosphere

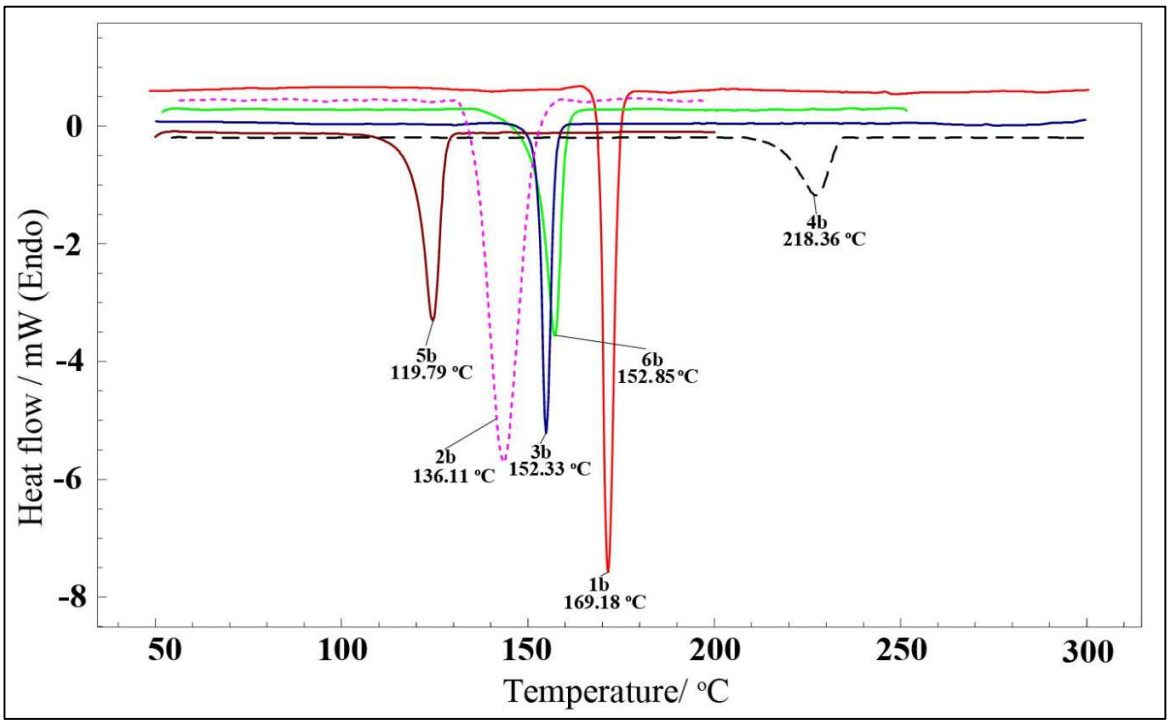


Fig 2. DSC curves of aryl esters 1b-6b at 10 ^{0}C heating rate in nitrogen atmosphere

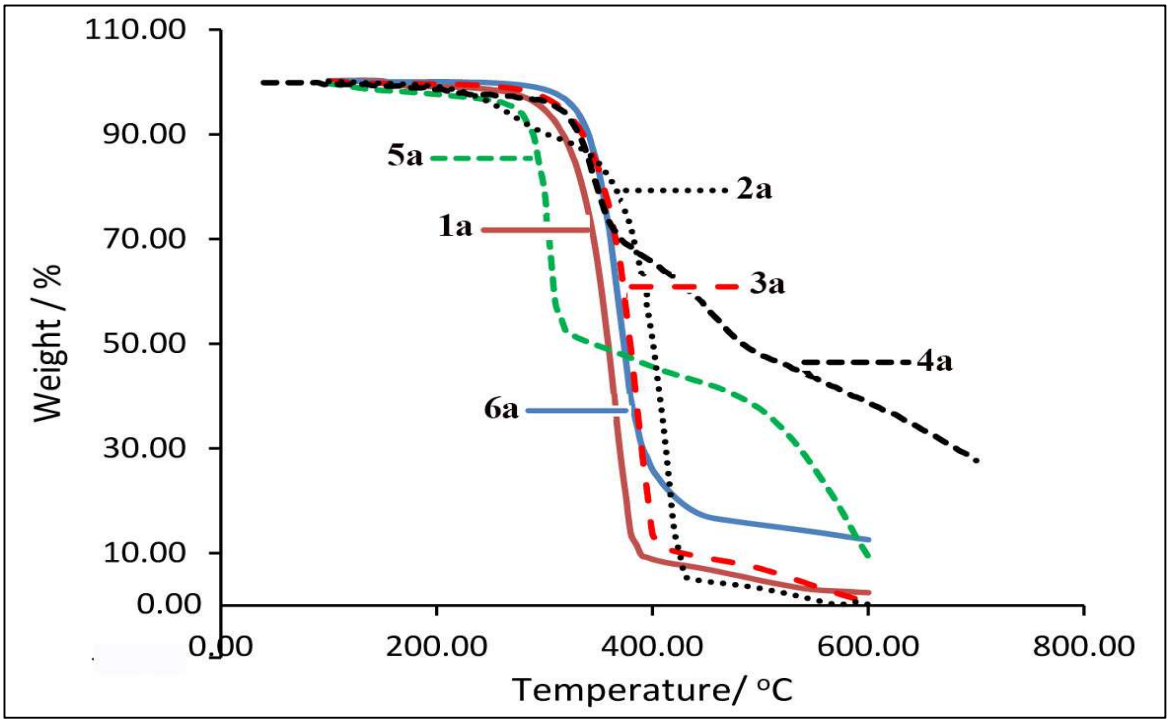


Fig.3 TG curves of aryl esters 1a-6a at 10 ^{0}C heating rate in nitrogen atmosphere

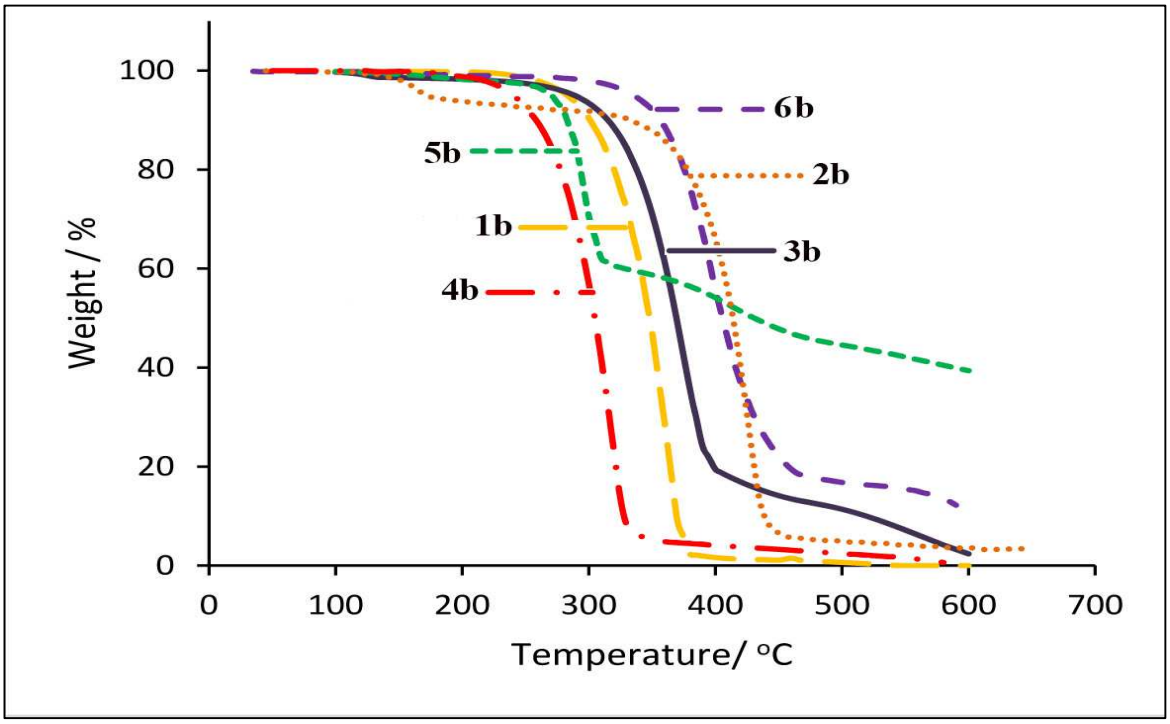


Fig 4. TG curves of aryl esters 1b-6bat 10 ^{0}C heating rate in nitrogen atmosphere

Table 1 DSC data of aryl esters

Aryl ester	Melting transition (T_m) ^{0}C (Endo)	ΔH, kJmol^{-1}	Entropy of transition ΔS, JK^{-1}mol^{-1}
1a	195.59	38.96	83.11
2a	152.93	20.55	48.24
3a	154.67	29.78	69.60
4a	257.34	58.03	109.39
5a	159.7	32.10	74.15
6a	156.97	41.92	97.46
1b	169.18	33.90	76.64
2b	136.11	36.38	88.88
3b	152.33	32.34	76.00
4b	218.36	18.22	37.07
5b	119.81	29.55	75.19
6b	152.85	45.62	107.09

Table 2 TGA data of aryl esters

Aryl ester	T_0 ^{o}C	T_{max} ^{o}C	Decom. Range ^{o}C	% Weight loss	% Residue at 500 ^{0}C
1a	255	363.8	255-405	89.9	4.8
2a	225	268.9	225-290	6.9	3.3
	330	411.8	330-430	82.2	-
3a	280	384.7	280-410	87.3	7.1
4a	285	346.1	285-380	28.5	47.8
	380	459.5	380-510	21.5	-
5a	270	301.6	270-325	43.6	37.5
	470	-	470-600	31.5	-
6a	290	366.2	290-450	82.1	15.4
1b	240	361.8	240-380	96.7	0.7
2b	135	-	135-185	4.82	4.8
	330	418.9	330-485	85.2	-
3b	255	374.1	255-405	78.4	11.4
4b	195	312.5	195-365	94.2	2.5
5b	255	295.0	255-315	35.6	44.6
	370	414.1	370-470	11.2	-
6b	305	398	305-480	80.1	16.8

Table 3 The kinetic parameters of aryl esters derived according to Anderson-Freeman method

Aryl ester	n	E_a, kJmol^{-1}	A, S^{-1}	ΔS^*, JK^{-1} mol^{-1}	R^2
1a	0.56	115.4	1.66×10^{7}	-113.0	0.993
2a	1.17	79.1	2.29×10^{5}	-147.3	0.975
	0.72	184.4	9.11×10^{11}	-22.9	0.984
3a	0.53	148.82	4.51×10^{9}	-66.7	0.979
4a	0.71	107.3	6.25×10^{6}	-120.9	0.978
	0.49	70.00	2.56×10^{2}	-206.3	0.999
5a	2.36	295.3	1.24×10^{25}	230.0	0.988
	-	-	-	-	-
6a	1.81	218	6.88×10^{15}	51.9	0.987
1b	0.28	100.4	9.14×10^{5}	-137.1	0.987
2b	-	-	-	-	-
	1.20	196.5	5.6×10^{12}	-7.8	0.983
3b	0.70	126.5	9.87×10^{7}	-98.3	0.998
4b	0.74	88.1	3.73×10^{5}	-143.9	0.991
5b	0.8	169.9	4.42×10^{13}	11.00	0.975
	1.06	89.3	1.24×10^{5}	-153.6	0.977
6b	1.13	120.2	1.22×10^{7}	-116.03	0.981

CONCLUSION

From DSC and TG study it is observed that thermal behaviour of aryl esters are affected by their molecular structure, nature, size and position of the substituents.

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