Effect of substitutions on thermal behavior of symmetric double Schiff bases of 1, 1'- bis (4-amino phenyl) cyclohexane

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ABSTRACT. Thermo gravimetric analyses of some symmetric double Schiff bases of 1, 1'- bis (4-amino phenyl) cyclohexane (SDSB-1 to SDSB-6) was carried out at 10⁰ C/min in nitrogen atmosphere. Schiff bases are thermally stable up to 200-285⁰C and followed two step degradation kinetic. Various kinetic parameters such as order of degradation (n), energy of activation (E_a), frequency factor (A) and entropy change (ΔS) were derived accordingly Anderson-Freeman method interpreted in light of nature of the substituents. The nature, size and position of substituents affected thermal properties of the Schiff bases.

1. INTRODUCTION

Thermal methods of analyses are most widely used to study industrially important products such as polymers, pharmaceuticals, metals, minerals, alloys, clays and various metal complexes etc. Jin et. al [1] have reported the thermal stabilities of the polyimide derived from 1,1' bis (4-amino phenyl) cyclohexane and its derivatives with PMDA, BTDA and HFDA. Polyamides showed glass transition ranging from 290-372 ⁰C, stable up to 500 ⁰C and 30% residue at 800 ⁰C. The glass transition temperature was found to increase with increasing methyl groups in 1, 1' bis (4-amino phenyl) cyclohexane because of steric restriction on the main chain rotation motion.

Schiff bases are useful as analytical reagents [2] fine chemicals, medical substrates and ligands for metal complexes having industrial importance as antifungal and biological applications [3]. They are also used as drug intermediates for the synthesis of drugs like antibiotics, antiallergic, antiphlogistic and antitumor [4]. Panchal et. al [5] have reported thermo gravimetric analysis of lanthanide coordination polymers with the Schiff base N,N'-di (o- hydroxy phenyl) terephthalaldehyde and determined final decomposition products. Aghera and Parsania [6] have reported thermo gravimetric analysis of symmetric double Schiff bases containing cardo group to understand the effect of different substituents on thermal stability, kinetic parameters of Schiff bases. Recently Gangani and Parsania [7-10] have reported thermo acoustical studies of various substituted symmetric double Schiff bases.

To our best knowledge no work has been reported on thermal behaviour of substituted Schiff bases, which encouraged us to study effect of hydroxy, chloro, phenoxy, nitro, N,N'- dimethyl and styrene substituents on thermal degradation kinetics.

2. EXPERIMENTAL

2.1. Materials

Solvents and chemicals used in the present investigation were of LR grade and used either as received or purified by fractional distillation. The Schiff bases were repeatedly recrystallized from appropriate solvent systems. 1, 1' Bis (4-aminophenyl) cyclohexane [Scheme-1] was synthesized and recrystallized according to reported work [2]. Symmetric double Schiff bases [Scheme-2] were synthesized by conventional and microwaves irradiation techniques [11-12].

Scheme-1 Synthesis of 1,1'- bis (4-amino phenyl)cyclohexane

Scheme-2 Syntheses of symmetric double Schiff bases

SDSB-1: R = -2 OH

SDSB-2: R = -4 Cl

SDSB-3: R = -3 OC₆H₅

SDSB-4: R = -3 NO₂

SDSB-5: R = -4 N(CH₃)₂

SDSB-6: R = 4-CH=CH-C₆H₅

2.2. Instrumentation and method

The Thermo gravimetric measurements were made on Perkin Elmer TGA Model No Pyris-I, at the heating rate of 10°C/min in nitrogen atmosphere.

3. RESULTS AND DISCUSSION

TG thermograms of SDSB-1 to SDSB-6 at the heating rate of 10°C/min in nitrogen atmosphere are presented in Figs.1 from which it is observed that SDSB-1 to SDSB-6 followed two steps decomposition reactions. Several temperature characteristic thermal properties such as initial decomposition temperature (IDT), temperature of 10 % weight loss (T_{10}), temperature of 50 % weight loss (T_{50}), final decomposition temperature (FDT), temperature of maximum weight loss (T_{max}) and the decomposition range were derived from these thermograms and are reported in Table 1. From which it is clear that Schiff bases are thermally stable up to about 200-285°C and different T_{max} values of 333-380°C suggested different degradation mechanism. Observed thermal stability order is SDSB-5 > SDSB-3 > SDSB-4 = SDSB-6 > SDSB-2 > SDSB-1.

Fig.-1 TG thermograms of SDSB-1 to SDSB-6 at the heating rate of 10°C/min in an N₂ atmosphere

Table-1: The TGA data of Schiff bases

Schiff bases	IDT °C	T ₁₀ °C	T ₅₀ °C	FDT °C	Decomposition Temp., °C	% Wt. Loss	T _{max} °C
SDSB-1	200.0	292.0	362.1	500.9 750	250-451 589-750	62.0 23.4	353.4 -
SDSB-2	239.0	287.5	352.0	379 560	239-379	66.3	355.9
SDSB-3	267	342.9	485.7	419.0 608	267-419 488-608	37.7 46.9	379.7 538.7
SDSB-4	250.0	319.5	358.7	372 589	250-372 480-589	35.4 46.4	350.3 565.8
SDSB-5	285.0	335.7	442.9	413 623	285-413 507-623	42.0 41.4	357.8 549.9
SDSB-6	250.0	217.4	467.4	367 620	250-367 474-620	24.2 44.3	333.1 554.0

Table-2: The kinetic parameters of Schiff bases derived according to Freeman-Anderson method

Schiff bases	n	E _a , kJ	A, S ⁻¹	ΔS*	γ
SDSB-1	3.3	315.02	2.94X10 ²⁴	217.4	0.998
SDSB-2	0.3	100.27	1.08x10 ⁶	-135.6	0.990
SDSB-3	0.2	482.70	9.43x10 ³⁶	456.4	0.953
	1.0	130.05	9.82x10 ⁵	-138.5	0.994
SDSB-4	0.7	135.19	1.48x10 ⁹	-75.5	0.993
	2.0	255.74	6.10x10 ¹³	10.4	0.995
SDSB-5	3.0	277.86	1.41x10 ²¹	153.7	0.989
	2.0	125.37	3.36x10 ⁵	-147.5	0.993
SDSB-6	0.4	449.80	1.83x10 ¹	-226.7	0.981
	0.3	180.40	7.28x10 ⁻³	-294.3	0.976

From this trend it is concluded that the nature, the position (Ortho, Meta and Para) and size of substituents affected thermal properties considerably. Associated kinetic parameters such as energy of activation (E_a), frequency factor (A), and order of reaction (n) were determined according to Anderson-Freeman method [13]. The least derived kinetic parameters are reported in Table 2. The entropy change (ΔS*) was determined at corresponding T_{max} and also reported Table 2. Schiff bases followed either fraction or integral order of degradation kinetics. The first step decomposition of SDSB-2, SDSB-3, SDSB-4 and SDSB-6 followed fraction order (0.3, 0.2, 0.7 and 0.4) degradation kinetics while SDSB-1 and SDSB-5 followed third order degradation kinetics. The second step decomposition of SDSB-3 followed first order kinetics while both SDSB-4 and SDSB-5 followed second order degradation kinetics. The second step decomposition of SDSB-6 followed 0.3 order degradation kinetics. The magnitude of E_a and A found different due to different nature and steric effect of the substituents. High magnitudes of these parameters suggest rigid nature of the Schiff bases.

A large and positive magnitudes of ΔS* confirmed less ordered transition states while negative magnitudes of ΔS* confirmed ordered transition state [13-16]. The side substituents are weak points in the Schiff bases which on heating forms free radicals which undergo further recombination, branching, rearrangement, cross linking reaction and further degrade at elevated temperatures.

4. CONCLUSION

Schiff bases possess fairly good thermal stability. The Schiff bases followed two step degradation kinetics either fraction order or integral order kinetics. The nature, size and position of the substituents affected thermal properties to considerably extent.

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