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Decomposition Kinetics of Some New Schiff Bases Derived From 4-Amino Benzoic Acid

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Abstract Some new Schiff bases have been synthesized from 4- amino benzoic acid and their thermal analysis have been carried out by TG technique. TG data of decomposition have been analysed for the kinetic parameters using Freeman-Carroll method. From the observed curves, various kinetic parameters such as order of degradation (n), energy of activation (E), frequency factor (A) and entropy change (ΔS) have been evaluated. Further, thermal stability of Schiff bases have been determined, which is found to depend on the type of substituent present in the compounds.

Keywords 4-Amino Benzoic Acid, Thermo Gravimetric Analysis, Differential Scanning Calorimeter, Kinetic Parameters, Thermal Stablity

1. Introduction

Schiff bases are condensation products of primary amines with carbonyl compounds. These bases are an important class of compounds because of the wide variety and potential applications of their industrial, analytical, medicinal, pharmaceutical and catalytical applications [1-6]. Further, Schiff bases are known to exhibit a broad spectrum of biological activities such as antimicrobial, antibacterial, antifungal and antiviral activities [7-10]. Owing to the wide application, in the present paper, some Schiff bases have been synthesized and studied their thermal properties.

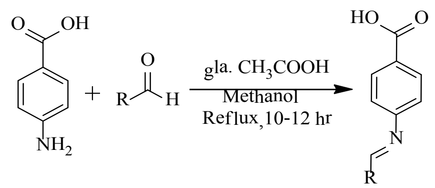
Thermal analysis has become an established method in the study of thermal behavior of materials and finds wide applications in various fields [11-15]. The thermal properties of epoxy resins [16], olive wood [17], fabrics [18] and composites [19] have also been studied by various workers using TGA. Kinetic study of thermal decomposition of various organic and inorganic compounds has also been reported by several workers [20-22]. In the present paper, thermal properties of some Schiff-bases of 5- amino benzoic acid have been reported.

2. Experimental

Thermal properties of following Schiff bases have been studied.

1. SB-1:4-{[4-methoxy-benzylidene]-amino}-benzoic acid
2. SB -2:4-(benzylidene-amino)-benzoic acid
3. SB -3:4-{[2-chloro-benzylidene]-amino}-benzoic acid
4. SB -4:4-{[furan-2-ylmethylene]-amino}-benzoic acid
5. SB -5:4-[3-phenyl-allylidene-amino]-benzoic acid
6. SB -6:4-{[2-hydroxy-benzylidene]-amino}-benzoic acid
7. S B-7:4-{[4-hydroxy-3-methoxy-benzylidene]-amino}-benzoic acid
8. SB -8:4-{[3-nitro-benzylidene)-amino]-benzoic acid

All these Schiff bases were synthesized according to the following scheme:



where R is different aromatic substitutions

The synthesized Schiff bases were recrystallised from ethanol. The purity of compounds was checked by thin layer chromatography. The General structure of Schiff base is given in Figure 1 and some physical constants and substituent R of all the synthesized Schiff bases are given in Table 1.

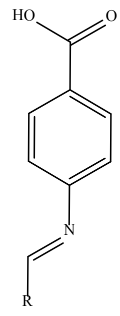


Figure 1. General structure of Schiff base

2.1. Instrumentation

Thermo gravimetric analysis (TGA), Differential thermal analysis (DTA) and differential scanning calorimetric (DSC) measurements were made on the instrument "Universal V 2.6 D TA instrument" at the heating rate of 10^o C/min in nitrogen atmosphere for all the Schiff bases.

2.2. Theory

Figures 2 and 3 show DSC and TGA/DTA of two compounds respectively. From TGA curves, various kinetic parameters can be evaluated by Freeman-Carroll [23] equation.

$$\ln (dC/dt)/\ln (1-C) = n-E/R\ [(1/T/(\Delta\ln(1-C)] \quad (1)$$

where C is the degree of conversion and is given by

$$C = 1-(W/W0) \quad (2)$$

W0 and W are the initial weight at t=0 and weight at any time t of the material, T is the temperature at absolute scale, n is order of reaction, E is energy of activation and R is gas constant.

The frequency factor A and entropy change ΔS can be determined by the following equations:

$$\ln E - \ln (RTs2) = \ln A - \ln\beta - E/RTs \quad (3)$$

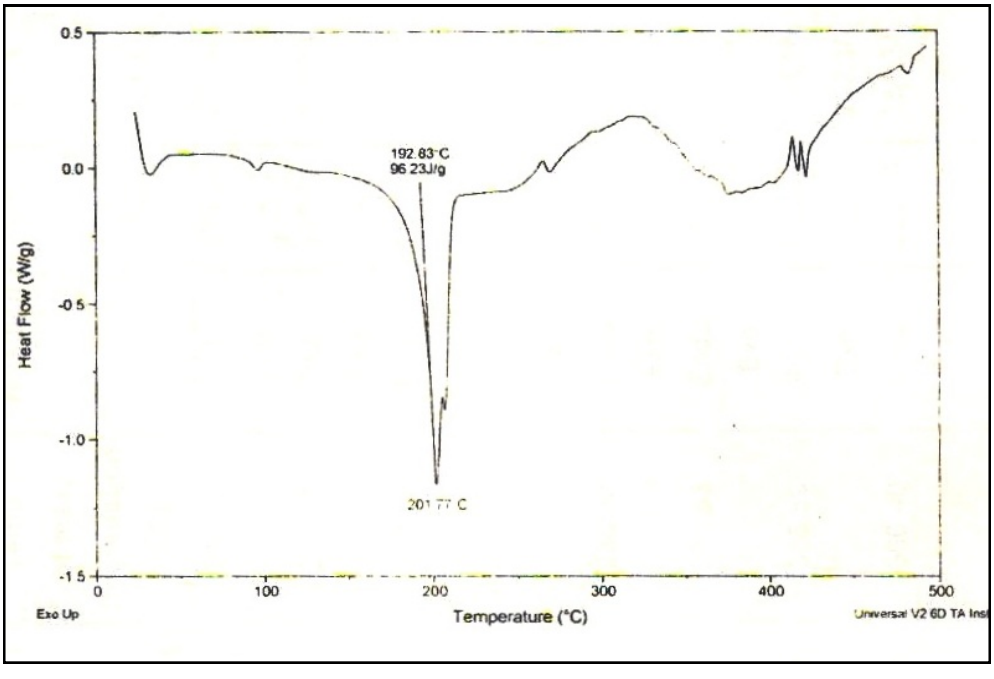
$$A = (kbT / h)\ e^{\Delta S/R} \quad (4)$$

where Ts is the temperature at which the rate of decomposition is maximum, β is heating rate, kb is Boltzmann constant and h is Planck's constant.

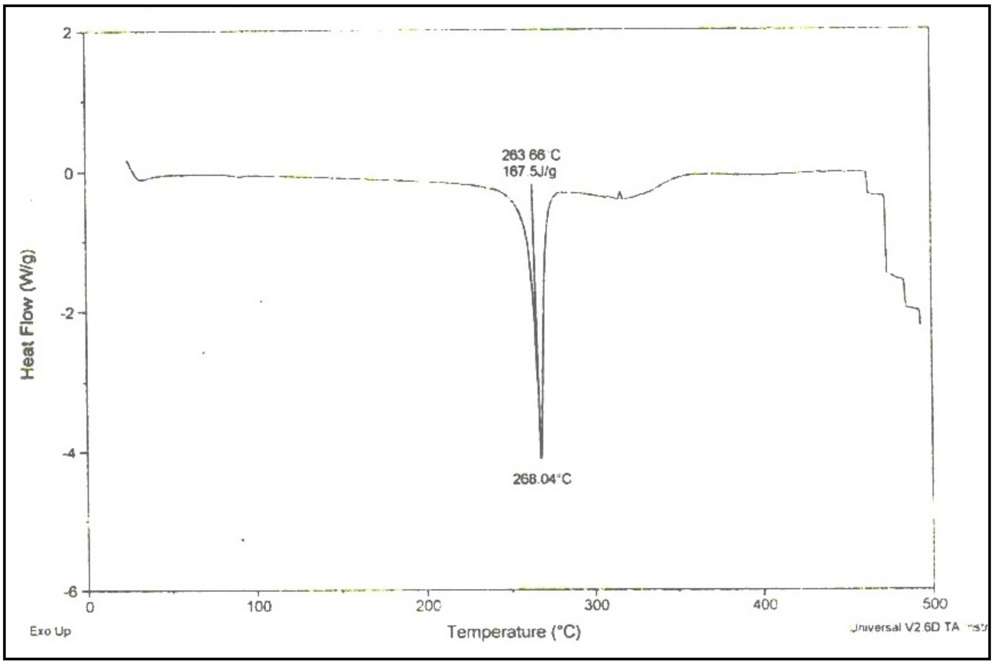
Table 1. Physical constants of Schiff bases.

Sr. No.	Code	R	M.F.	M. Wt. g	R_f* Value	M.P. °C	Yield %
1.	SB-1	4-OCH_3-C_6H_4-	$C_{15}H_{13}NO_3$	255.27	0.61*	186	62
2.	SB-2	-C_6H_4-	$C_{14}H_{11}NO_2$	225.24	0.51*	170	45
3.	SB-3	3-Cl-C_6H_4	$C_{14}H_{10}NO_2Cl$	256.69	0.45*	202	52
4.	SB-4	-CH=CH-CH_2-C_6H_4-	$C_{12}H_9NO_3$	215.20	0.48+	212	59
5.	SB-5	-C_4H_4O	$C_{16}H_{13}NO_2$	251.28	0.58+	172	63
6.	SB-6	2-OH- C_6H_4-	$C_{14}H_{11}NO_3$	241.24	0.41*	268	57
7.	SB-7	4-OH,3- OCH_3-C_6H_4-	$C_{15}H_{13}NO_4$	271.27	0.52+	115	55
8.	SB-8	3-NO_2-C_6H_4-	$C_{13}H_9N_2O_4$	270.23	0.32+	250	65

* Hexane : Ethyl acetate (2.5+7.5)
+ Acetone : Benzene (4.0+6.0)

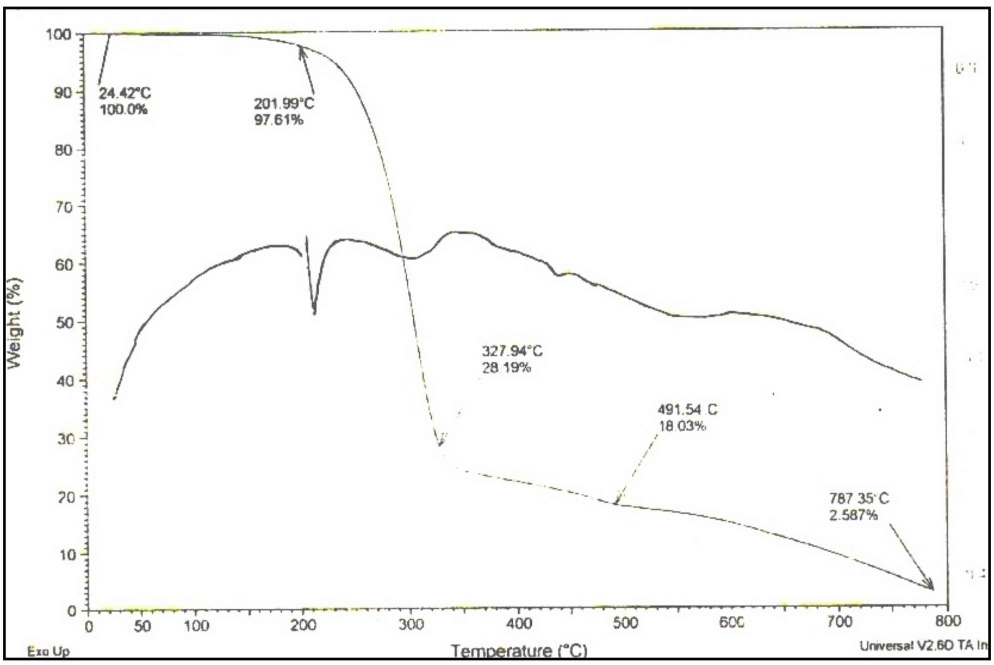


[A]



[B]

Figure 2. The DSC graph of [A] SB-3 and [B] SB-6.



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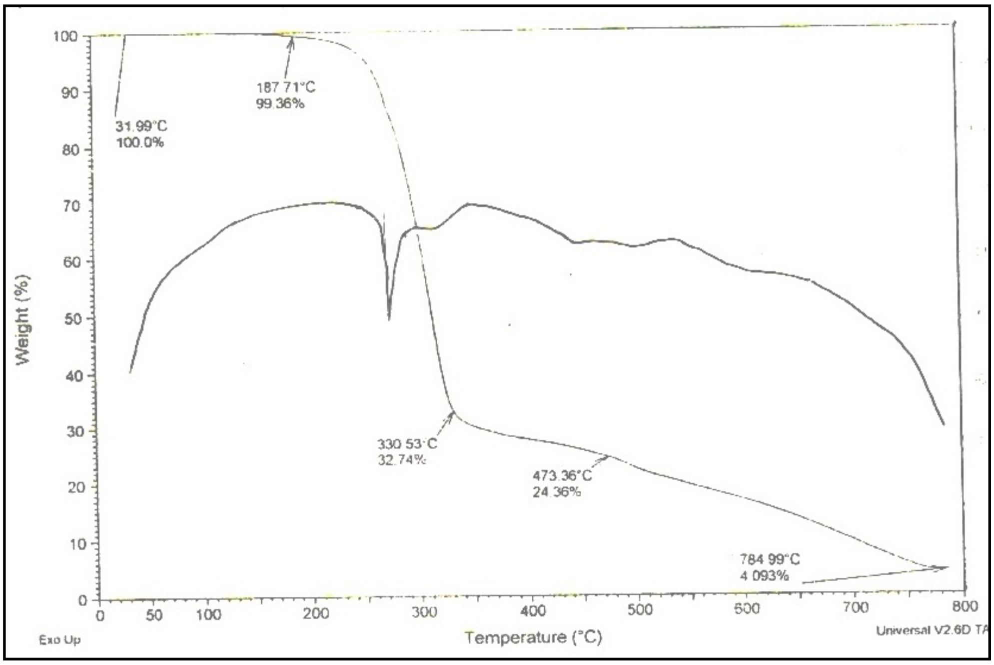
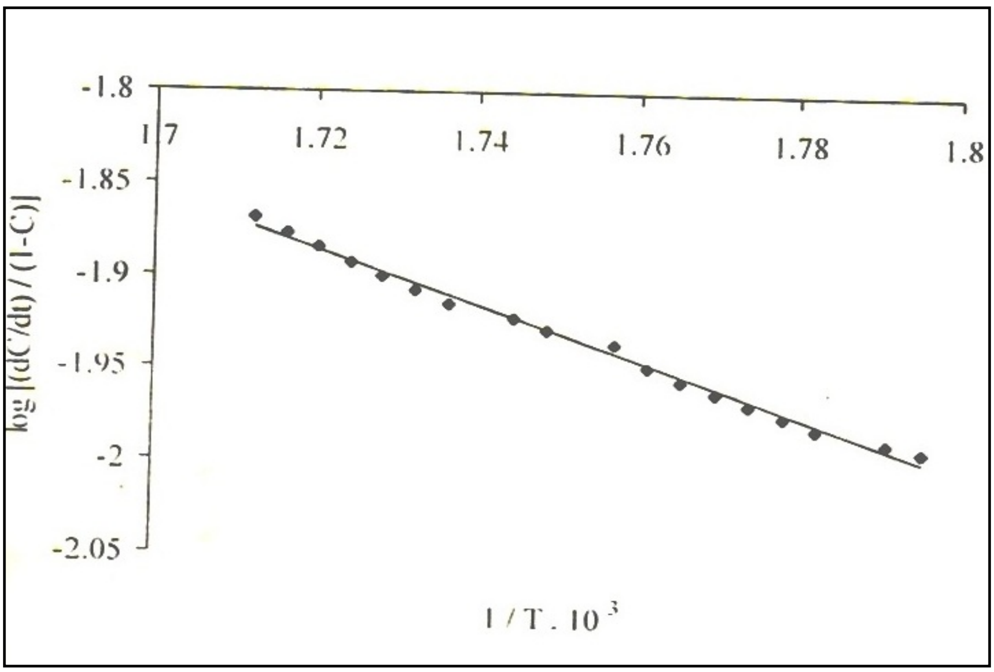


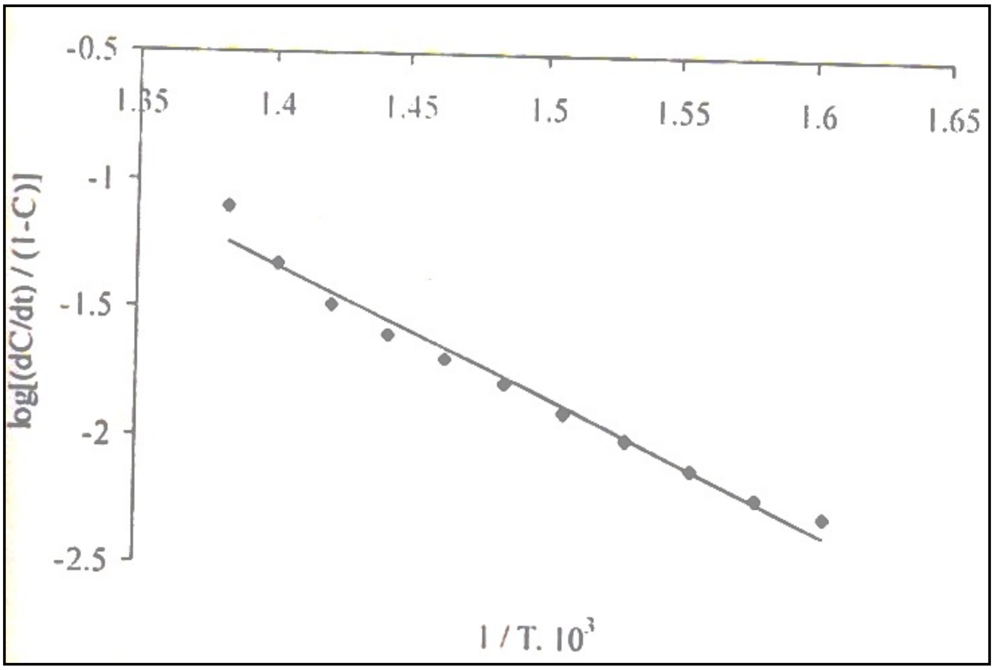
[B]

Figure 3. The TGA /DTA of [A] SB-3 and [B] SB-6

A plot of left hand side of ln (dC/dt)/ln (1-C) against (1/T) gives a straight line (as shown in Figure 4) with a slope equal to -E/R and the intercept is equal to n.



[A]



[B]

Figure 4. The Freeman-Carroll plots for [A] SB-1 and [B] SB-2.

Table 2. TGA data for synthesized Schiff bases.

Comp. Code	Amt. (mg.)	Initial Decomp. Temp. (^oC)	Decomp. Range (^oC)	% Wt. left	Residual Wt. Loss (mg.)	Max. Degradt. Temp. (^oC)
SB-1	13.7546	230.00	230-340	15.7000	2.1595	340.92
SB-2	12.0487	189.00	189-267	2.7850	0.3355	266.91
SB-3	10.7575	201.99	201-328	2.5870	0.2783	327.94
SB-4	13.8432	24.43	84-273	25.6800	3.5549	273.40
SB-5	6.0113	24.37	118-338	0.2980	0.0017	338.32
SB-6	9.3160	187.71	188-330	4.0930	0.3813	330.53
SB-7	15.2748	130.57	131-366	8.2960	1.2672	365.59
SB-8	11.0240	146.16	260-360	5.2271	0.5762	360.40

Table 3. The kinetic parameters for Schiff bases

Comp. code	n	E (kJ)	A (Sec^{-1})	ΔS^o (kJ^{-1})
SB-1	2.20	129.42	22.30	226.29
SB-2	1.70	91.17	24.9×10^5	129.97
SB-3	1.00	89.96	21.9×10^6	112.19
SB-4	2.00	26.80	2.41	248.15
SB-5	1.05	27.95	5.93	238.11
SB-6	1.45	103.21	1.32×10^2	211.89
SB-7	1.15	105.64	59.40	217.29
SB-8	1.80	85.29	11.85	231.98

3. Results and Discussion

From the thermo grams (Figure 3), various thermal properties such as initial decomposition temperature (IDT), the decomposition temperature range and the maximum degradation along with the percentage weight loss and Exo / Endo transitions were evaluated and are reported in Table 2.

It is observed from Table 2 that stability of Schiff bases decrease in order: SB-1> SB-3> SB-2> SB-6> SB-8> SB-7> SB-5> SB-4. The stability depends on the substitution group. SB-4 and SB-5 bases are less stable due to the presence of cinnamyl and furfurayl groups respectively whereas methoxy substitution increases the stability to maximum in the studied Schiff bases. For all the Schiff bases, except SB-4 and SB-1, weight loss is less than 10 %. The variation in the trend of thermal decomposition might be interpreted by taking into account some intermolecular interactions (structural as well as electronic) and also because of several experimental factors.

Further, various kinetic parameters, such as order of the degradation (n), energy of activation (E), frequency factor (A) and entropy change (ΔS) have also been calculated and are reported in Table 3 along with correlation coefficient. It is evident from Table 3 that order of reaction is maximum for SB-1. For rest of the Schiff bases, the values are less than two but more than one except SB-3.

For all the Schiff bases, energy of activation (E) decreases in the following order: SB -1> SB-7> SB-6> SB-2> SB-3> SB-8> SB-5> SB-4. The frequency factor (A) is observed to be maximum for SB-3 and minimum for SB-4. Over all, wide range of A is observed.

Further, change in entropy (ΔS^0) for all these reactions were also calculated by equation 4 and are reported in Table 3. The entropy change decreases in the order: SB-4> SB-5> SB-8> SB-1> SB-7> SB-6> SB-2> SB-3. For all the Schiff bases, change in entropy values is found to be positive. The positive values of ΔS^0 indicates that the transition state is less ordered than the original compound [24] .

4. Conclusion

The degradation in the studied Schiff bases is single step process with different order of reaction. Further, thermal stability depends upon the type of substituent present. It is observed that in the above studied Schiff bases, the presence of methoxy group (as in HPI-1) increases the stability whereas cinnamyl (as in SB-4and furfurayl groups (as in SB-5) decreases the stability.

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