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SHORT COMMUNICATION

Kinetics of thermal degradation of cyanopyridine derivatives

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ABSTRACT

Some new cyanopyridine derivatives have been synthesized and characterization of the synthesized compounds was done by IR, NMR and mass spectral data. The thermal properties of these compounds were studied by thermogravimetry. The thermal stability, melting temperature and some kinetic parameters such as energy of activation, frequency factor, order of reaction and entropy of activation were evaluated from thermograms. The degradation is single step process for some compounds whereas for others, it is multi step process.

***Keywords*:** Cyanopyridine derivatives; thermogravimetry; thermal stability; kinetic parameters

1. INTRODUCTION

Cyanopyridines attract attention to medicinal chemists due to their pharmacological activities. Literature survey shows that large array of cyanopyridine derivatives possess a variety of biological activities, such as antifungal [1], antihistaminic activity [2], insecticidal activity [3], antitubercular and antimicrobial [4], etc. Further, some of these derivatives have different applications in various fields like pharmaceutical, photo and agro industries [5-7].

The study of thermal properties provides information about various material properties such as melting, polymorphic transformations, thermal stability, kinetics of degradation, crystallinity etc.

Thus, it would be interesting to study the thermal properties of these compounds. The obtained thermal data may be useful for medicinal chemists to select a lead molecule for a drug. In the present work, thermal analysis of some newly synthesized cyanopyridine derivatives were carried out by thermogravimetry (TG). By thermograms, thermal stability, melting points and various kinetic parameters such as order of degradation, energy of activation, frequency factor and entropy change have been evaluated.

2. EXPERIMENTAL

The reaction scheme for the synthesis of various cyanopyridine derivatives is shown in Figure 1. The structures of all the synthesized compounds were confirmed by IR, ^{1}H NMR and mass spectral data. The IR spectra were recorded by SHIMADZU-FTIR-8400 Spectrophotometer in the frequency range of 4000-400 cm^{-1} by KBr powder method. The NMR spectra were recorded by BRUKER Spectrometer (400 MHz) using internal reference TMS and solvent $CDCl_3/D_6$-DMSO. The Mass spectra were recorded by GCMS-SHIMADZU-QP2010.

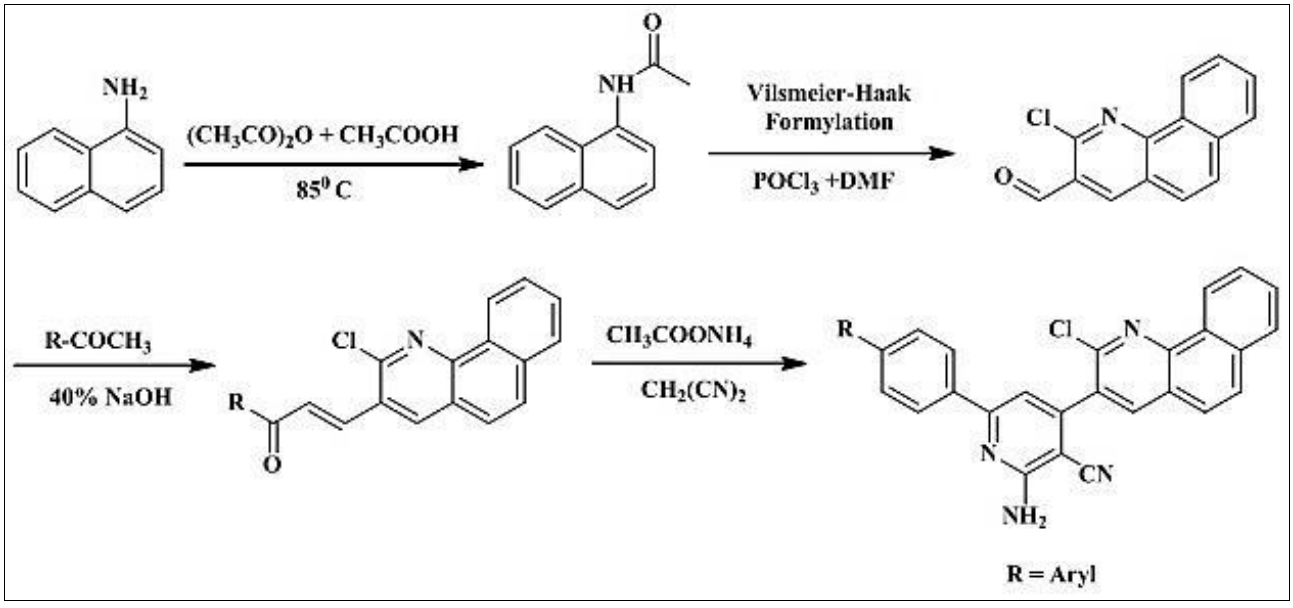

Figure 1. Reaction scheme of cyanopyridines

3. RESULTS AND DISCUSSION

The physical properties of all the synthesized compounds are given in Table 1 with their side chain substitution.

Table 1. Physical parameters of cyanopyridine derivatives

Comp. code	R	M.W.	M.P. °C	Yield %
CP-1	4-OCH_3-C_6H_4-	436.8	221	70
CP-2	4-CH_3-C_6H_4-	420.8	180	68
CP-3	4-Br-C_6H_4-	485.7	214	71
CP-4	4-NH_2-C_6H_4-	421.8	208	65
CP-5	4- NO_2-C_6H_4-	451.8	187	69
CP-6	3-OH-C_6H_4-	422.8	235	67
CP-7	4-Cl-C_6H_4-	441.3	234	72
CP-8	3- NO_2-C_6H_4-	451.8	201	63
CP-9	4-OH-C_6H_4-	422.8	229	65
CP-10	H-C_6H_4-	406.8	162	73

3. 1. Spectral Data

CP-1 ***IR* (*cm*$^{-1}$, *KBr*):** 2943.47 (asym. C-H str.), 1429.30 (asym. C-H def.), 1371.43 (sym. C-H def.), 3066.92 (sym. aromatic C-H str.), 1514.17 (aromatic C=C str.), 2195.07 (C≡N str.)1660.77 (C=N str.), 1257.63 (C-N str.), 1226.77 (asym. C-O-C str.), 1018.45 (sym. C-O-C str.), 690.54 (C-Cl str.), 3313.82 (N-H str.), 1591.33 (N-H def.), ***^{1}H NMR (DMSO-d_6)* δ*(ppm)*:** 3.83 (3H, singlet, -OCH_3), 3.49 (2H, singlet, -NH_2), 7.09-7.12 (2H, doublet, Ar-CH), 7.50-7.54 (1H, triplet, Ar-CH), 7.66-7.76 (2H, doublet, Ar-CH), 7.83-7.99 (2H, multiplet, Ar-CH), 8.07-8.10 (2H, multiplet, Ar-CH), 8.37 (1H, singlet, Ar-CH), 8.51(2H, doublet, Ar-CH), ***MS*: *(m/z)*** = 436.8

CP-2 ***IR* (*cm*$^{-1}$, *KBr*):** 2943.42 (asym. C-H str.), 1429.34 (asym. C-H def.), 1371.23 (sym. C-H def.), 3066.72 (sym. aromatic C-H str.), 1588.33 (aromatic C=C str.), 2201.23 (C≡N str.) 1660.72 (C=N str.), 1257.63 (C-N str.), 1226.77 (asym. C-O-C str.), 1018.45 (sym. C-O-C str.), 698.81 (C-Cl str.), 3347.63 (N-H str.), 1591.23 (N-H def.), ***^{1}H NMR (DMSO-d_6)* δ*(ppm)*:** 1.21 (3H, singlet, -CH_3), 3.44 (2H, singlet, -NH_2), 7.08-7.11 (2H, doublet, Ar-CH), 7.52-7.56 (1H, triplet, Ar-CH), 7.68-7.72 (2H, doublet, Ar-CH), 7.85-7.96 (2H, multiplet, Ar-CH), 8.09-8.12 (2H, multiplet, Ar-CH), 8.36 (1H, singlet, Ar-CH), 8.51 (2H, doublet, Ar-CH), ***MS*: *(m/z)*** = 420.8

CP-3 ***IR* (*cm*$^{-1}$, *KBr*):** 2943.41 (asym. C-H str.), 1429.74 (asym. C-H def.), 1371.57 (sym. C-H def.), 3066.34 (sym. aromatic C-H str.), 1512.41 (aromatic C=C str.), 2198.45 (C≡N str.) 1660.24 (C=N str.), 1257.14 (C-N str.), 1226.02 (asym. C-O-C str.), 1018.21 (sym. C-O-C str.), 709.13 (C-Cl str.), 3332.09 (N-H str.), 1591.56 (N-H def.), ***^{1}H NMR (DMSO-d_6)* δ*(ppm)*: *MS*:** 3.40 (2H, singlet, -NH_2), 7.12-7.16 (2H, doublet, Ar-CH), 7.52-7.57 (1H, triplet,

Ar-CH), 7.62-7.69 (2H, doublet, Ar-CH), 7.85-7.98 (2H, multiplet, Ar-CH), 8.09-8.12 (2H, multiplet, Ar-CH), 8.36 (1H, singlet, Ar-CH), 8.53 (2H, doublet, Ar-CH), ***(m/z)*** = 485.7

CP-4 *IR* (*cm*$^{-1}$, *KBr*): 2943.44 (asym. C-H str.), 1429.77 (asym. C-H def.), 1371.11 (sym. C-H def.), 3066.18 (sym. aromatic C-H str.), 1524.27 (aromatic C=C str.), 2212.74 (C≡N str.) 1660.77 (C=N str.), 1257.63 (C-N str.), 1226.77 (asym. C-O-C str.), 1018.45 (sym. C-O-C str.), 718.78 (C-Cl str.), 3318.31 (N-H str.), 1591.70 (N-H def.), ***^{1}H NMR (DMSO-d_6)*** ***δ(ppm)*:** 3.46 (4H, singlet, -NH_2), 7.10-7.14 (2H, doublet, Ar-CH), 7.52-7.57 (1H, triplet, Ar-CH), 7.68-7.71 (2H, doublet doublet, Ar-CH), 7.83-7.90 (2H, multiplet, Ar-CH), 8.11-8.15 (2H, multiplet, Ar-CH), 8.37 (1H, singlet, Ar-CH), 8.56 (2H, doublet, Ar-CH), ***MS*: *(m/z)*** = 421.8

CP-5 *IR* (*cm*$^{-1}$, *KBr*): 2943.78 (asym. C-H str.), 1429.44 (asym. C-H def.), 1371.13 (sym. C-H def.), 3066.72 (sym. aromatic C-H str.), 1503.15 (aromatic C=C str.), 2208.31 (C≡N str.) 1660.27 (C=N str.), 1257.67 (C-N str.), 1226.74 (asym. C-O-C str.), 1018.25 (sym. C-O-C str.), 695.42 (C-Cl str.), 3321.26 (N-H str.), 1591.46 (N-H def.), ***^{1}H NMR (DMSO-d_6)*** ***δ(ppm)*:** 3.44 (2H, singlet, -NH_2), 7.06-7.14 (2H, doublet, Ar-CH), 7.53-7.59 (1H, triplet, Ar-CH), 7.62-7.73 (2H, doublet doublet, Ar-CH), 7.85-7.92 (2H, multiplet, Ar-CH), 8.07-8.11 (2H, multiplet, Ar-CH), 8.32 (1H, singlet, Ar-CH), 8.50 (2H, doublet, Ar-CH), ***MS*: *(m/z)*** = 451.8

CP-6 *IR* (*cm*$^{-1}$, *KBr*): 2943.47 (asym. C-H str.), 1429.21 (asym. C-H def.), 1371.77 (sym. C-H def.), 3066.66 (sym. aromatic C-H str.), 1530.16 (aromatic C=C str.), 2226.78 (C≡N str.) 1660.29 (C=N str.), 1257.21 (C-N str.), 1226.21 (asym. C-O-C str.), 1018.01 (sym. C-O-C str.), 685.28 (C-Cl str.), 3306.55 (N-H str.), 1591.13 (N-H def.), ***^{1}H NMR (DMSO-d_6)*** ***δ(ppm)*:** 3.46 (2H, singlet, -NH_2), 7.20 (1H, singlet, Ar-CH), 7.52-7.56 (1H, triplet, Ar-CH), 7.69-7.73 (2H, doublet doublet, Ar-CH), 7.83-7.91 (3H, multiplet, Ar-CH), 8.09-8.13 (2H, multiplet, Ar-CH), 8.36 (1H, singlet, Ar-CH), 8.53 (2H, doublet, Ar-CH), 9.14 (1H, singlet, -OH), ***MS*: *(m/z)*** = 422.8

CP-7 *IR* (*cm*$^{-1}$, *KBr*): 2943.27 (asym. C-H str.), 1429.46 (asym. C-H def.), 1371.88 (sym. C-H def.), 3066.72 (sym. aromatic C-H str.), 1522.09 (aromatic C=C str.), 2205.61 (C≡N str.) 1660.97 (C=N str.), 1257.23 (C-N str.), 1226.74 (asym. C-O-C str.), 1018.37 (sym. C-O-C str.), 698.60 (C-Cl str.), 3319.42 (N-H str.), 1591.27 (N-H def.), ***^{1}H NMR (DMSO-d_6)*** ***δ(ppm)*:** 3.45 (2H, singlet, -NH_2), 7.12-7.15 (2H, doublet, Ar-CH), 7.50-7.54 (1H, triplet, Ar-CH), 7.62-7.66 (2H, doublet doublet, Ar-CH), 7.82-7.90 (2H, multiplet, Ar-CH), 8.11-8.17 (2H, multiplet, Ar-CH), 8.35 (1H, singlet, Ar-CH), 8.53 (2H, doublet, Ar-CH), ***MS*: *(m/z)*** = 441.3

CP-8 *IR* (*cm*$^{-1}$, *KBr*): 2943.42 (asym. C-H str.), 1429.30 (asym. C-H def.), 1371.43 (sym. C-H def.), 3066.92 (sym. aromatic C-H str.), 1514.17 (aromatic C=C str.), 2201.23 (C≡N str.), 1660.47 (C=N str.), 1257.63 (C-N str.), 1226.25 (asym. C-O-C str.), 1018.38 (sym. C-O-C str.), 712.16 (C-Cl str.), 3311.33 (N-H str.), 1591.34 (N-H def.), ***^{1}H NMR (DMSO-d_6)*** ***δ(ppm)*:** 3.48 (2H, singlet, -NH_2), 7.22 (1H, singlet, Ar-CH), 7.50-7.54 (1H, triplet, Ar-CH), 7.66-7.76 (2H, doublet doublet, Ar-CH), 7.80-7.92 (3H, multiplet, Ar-CH), 8.07-8.10 (2H, multiplet, Ar-CH), 8.37 (1H, singlet, Ar-CH), 8.51(2H, doublet, Ar-CH), ***MS*: *(m/z)*** = 451.8

CP-9 *IR* (*cm*$^{-1}$, *KBr*): 2943.34 (asym. C-H str.), 1429.26 (asym. C-H def.), 1371.11 (sym. C-H def.), 3066.26 (sym. aromatic C-H str.), 1526.41 (aromatic C=C str.), 2207.86 (C≡N str.), 1660.27 (C=N str.), 1257.89 (C-N str.), 1226.55 (asym. C-O-C str.), 1018.24 (sym. C-O-C str.), 688.53 (C-Cl str.), 3309.22 (N-H str.), 1591.68 (N-H def.), ***^{1}H NMR (DMSO-d_6)*** ***δ(ppm)*:** 3.47 (2H, singlet, -NH_2), 7.13-7.16 (2H, doublet, Ar-CH), 7.52-7.56 (1H, triplet, Ar-CH), 7.62-7.69 (2H, doublet doublet, Ar-CH), 7.84-7.91 (2H, multiplet, Ar-CH), 8.08-8.12 (2H, multiplet, Ar-CH), 8.35 (1H, singlet, Ar-CH), 8.54 (2H, doublet, Ar-CH), 9.18 (1H, singlet, -OH), ***MS*: *(m/z)*** = 422.8

CP-10 *IR* (*cm*$^{-1}$, *KBr*): 2943.42 (asym. C-H str.), 1429.30 (asym. C-H def.), 1371.43 (sym. C-H def.), 3066.92 (sym. aromatic C-H str.), 1521.05 (aromatic C=C str.), 2218.39 (C≡N str.), 1660.23 (C=N str.), 1257.61 (C-N str.), 1226.66 (asym. C-O-C str.), 1018.79 (sym. C-O-C str.), 701.37 (C-Cl str.), 3309.22 (N-H str.), 1591.33 (N-H def.), ***^{1}H NMR (DMSO-d_6)*** ***δ(ppm)*:** 3.49 (2H, singlet, -NH_2), 7.03-7.08 (3H, doublet, Ar-CH), 7.50-7.54 (1H, triplet, Ar-CH), 7.66-7.76 (2H, doublet doublet, Ar-CH), 7.86-7.90 (2H, multiplet, Ar-CH), 8.07-8.10 (2H, multiplet, Ar-CH), 8.37 (1H, singlet, Ar-CH), 8.51(2H, doublet, Ar-CH), ***MS*: *(m/z)*** = 406.8

3. 2. Thermal Analysis

The TG thermo gram of compound CP-2 is given in Figure 2. Table 2 shows decomposition range and residual weight of cyanopyridine derivatives. Out of ten compounds, degradation is single step process for some compounds whereas for others, it is multi step process. The order of reaction is quite different in different steps for different cyanopyridines. For single step degradation compound, order of reaction varies from 0.38 to 10.68, whereas for multi steps it varies from 0.25 to 6.4.

Table 2. Decomposition range and residual weight of cyanopyridine derivatives.

Comp. Code	Decomp. Range (°C)	% Wt. loss	Residual Wt. Loss (mg)
CP-1	200-700	57.42	3.074
CP-2	150-300	92.65	4.026
CP-3	200-700	42.90	2.417
CP-4	200-705	46.80	2.559
CP-5	150-897	42.57	2.140
CP-6	200-700	52.14	1.902
CP-7	100-599	47.80	2.844
CP-8	185-800	47.88	1.923
CP-9	205-750	40.57	2.410
CP-10	150-600	35.74	1.559

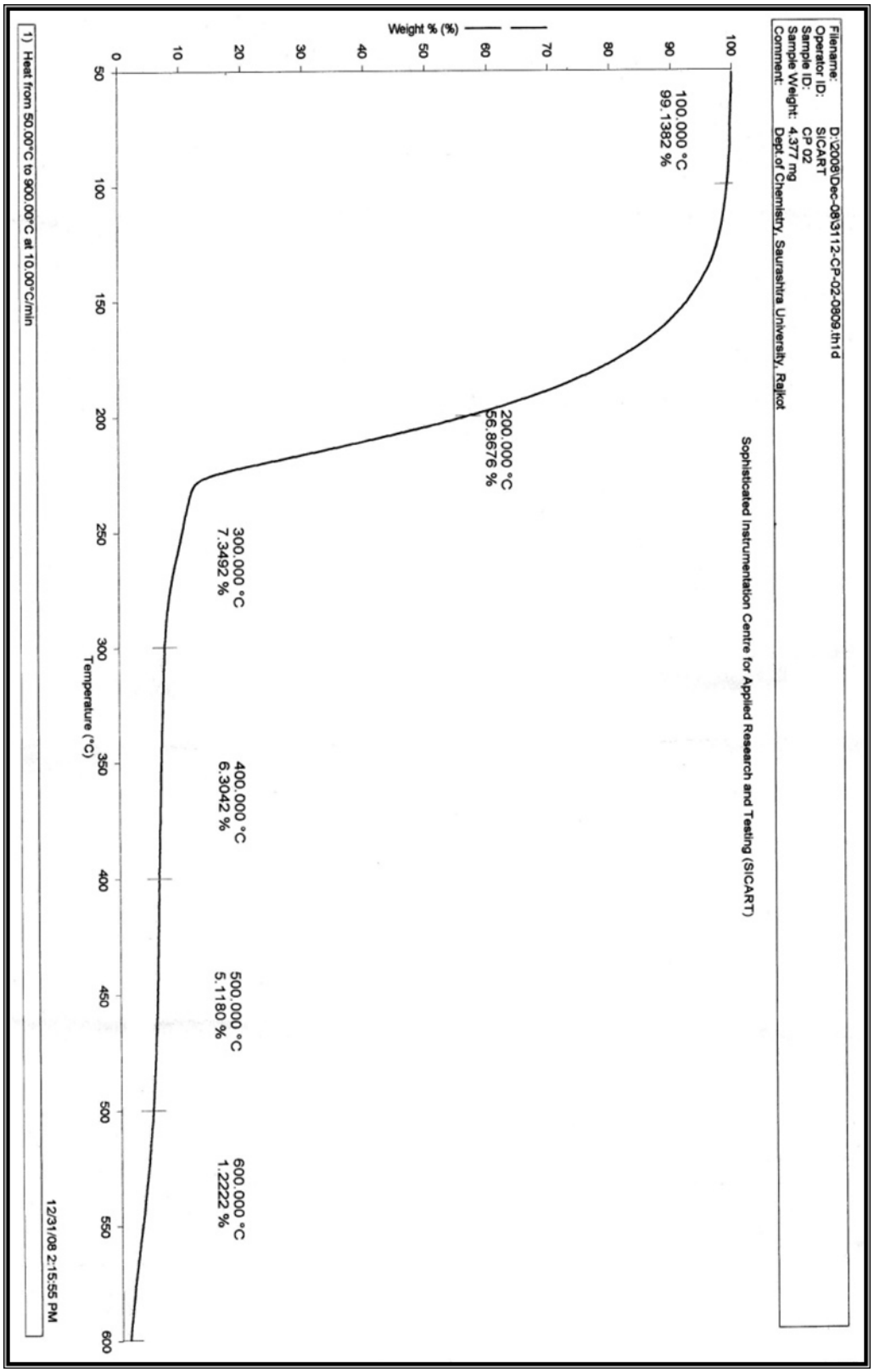

Figure 2. TGA of CP-2

Table 3 shows the kinetic parameters of cyanopyridine derivatives. For single step degradation compounds, energy of activation (*E*) is maximum for CP-2 and minimum for CP-8. The frequency factor (*A*) also varies in the same order. For multi-step degradation compounds, in first and second steps, energy of activation is found to be maximum for CP-9 in second step and minimum for the second step of CP-4. The frequency factor A follows the same order. The entropy values are both positive and negative for different compounds. The positive entropy indicates that the transition state is less ordered than the original compound whereas negative entropy corresponds to an increase in the order of transition state than the reactants.

Table 3. The kinetic parameters of cyanopyridine derivatives.

Comp. code	n	E [kJ·mol^{-1}]	A [s^{-1}]	ΔS [J·mol^{-1}·K^{-1}]
CP-1	2.25	67.49	1.68 x 10^{10}	103.13
CP-1	1.39	65.63	3.02 x10^{03}	-32.68
CP -2	0.38	276.63	1.02 x 10^{17}	225.43
CP -3	1.90	128.35	1.14 x 10^{25}	349.86
CP -4	0.25	56.701	6.25 x 10^{09}	96.01
CP -4	1.17	45.73	8.74 x 10^{01}	-48.91
CP -4	2.50	241.86	7.81 x10^{12}	60.49
CP -5	1.79	153.49	1.11 x 10^{17}	230.93
CP -6	6.60	205.42	1.39 x 10^{37}	619.54
CP -7	7.88	97.49	2.39 x 10^{17}	241.16
CP -8	10.68	17.33	1.14 x 10^{02}	-52.43
CP -9	2.30	73.09	3.47 x 10^{11}	128.57
CP -9	6.40	854.21	2.68 x 10^{84}	1519.72
CP -10	5.10	107.33	1.69 x 10^{22}	335.19

CP-7 is most unstable whereas CP-9 is very stable. All the studied compounds have a common moiety with different constituents as side chain. Thus, the stability of the compounds depends upon the substituent group. The hydroxyl group at *para*- position increases the stability is highest whereas chloro- group decreases the stability.

4. CONCLUSION

Out of ten compounds, degradation is single step process for some compounds whereas for others, it is multi step process. Thermal stability is much affected by the nature and position of the substitutions present in the studied compounds. The hydroxyl group at para position increases the stability is highest whereas chloro- group decreases the stability.

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