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Thermal analysis of some novel Chalcones

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Abstract:

Decomposition characteristics of some newly synthesized chalcones have been studied by thermo gravimetric and differential scanning calorimetric analysis. From thermo grams, some kinetics parameters of decomposition were also evaluated. It is observed that thermal stability and decomposition kinetics depends on nature and position of substituent present in these compounds.

Keywords: Chalcones; thermal gravimetric analysis; differential scanning calorimetry; thermal stability; kinetic parameters.

Introduction:

Studies on thermal properties of substances are of great importance from both scientific and practical point of view. Scientific and technological achievements together with demands based on industrial requirement have permitted the development of various types of materials that can withstand at much higher temperatures and more corrosive environments.

Among several instruments and techniques, thermal analysis has grown rapidly in recent years. Thermal analysis has been used to determine the physical and chemical properties of various types of materials [1-6]. Both quantitative and qualitative analysis can be carried out and one can identify and characterize the samples by qualitative investigations of their thermal behaviors. Current areas of applications include environmental measurements, composition analysis, product reliability, stability, chemical reaction and dynamic properties. Further, various reversible and nonreversible reactions [7-9], the decomposition of molecules absorbed on a surface, phase transitions etc. can also be studied. This analysis also provides the measurement of overall kinetic parameters of thermally simulated reactions which permit a deeper insight in to the mechanism of high energetic compounds.

Thermal analysis includes a group of techniques in which specific physical properties of a material are measured as a function of time or temperature. The well facilated instrument can measure transition temperature, weight losses, and energy of transition, dimensional changes, modulus changes and viscoelectric properties. Some of commonly used thermal techniques are Differential Scanning calorimetry, Differential thermal analysis, Thermo gravimetric analysis, Evolved gas detection, Evolved gas analysis etc.

Literature survey shows that thermal analysis has been reported for a number of materials in various fields such as pharmaceutical industry [10, 11], forensic science applications [12, 13], chemistry [14, 15], food industry [16, 17], ceramics [18, 19], polymer industry [20, 21] etc.

In the present work, thermal properties of some newly synthesized chalcones derivatives have been studied by Thermo gravimetric (TG) and Differential scanning calorimetric (DSC) techniques. From TG thermo grams, the thermal stability and various kinetic parameters such as order of the degradation, energy of activation, frequency factor and entropy change have been evaluated. DSC gives information about purity and melting points of compounds.

Experimental:

Synthesis:

Some new chalcones are synthesized from two different starting materials. In both serried, the central moiety is different but substitutions are same. Figure 1 shows the general structures of compounds of both the series and various physical parameters along with their substitutions are listed in Table 1.

Thermal Analysis:

Thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were made using instrument "Pyris-1, Perkin Elmer Thermal analysis" at the heating rate of 10^0C/min in nitrogen atmosphere for all the synthesized chalcones.

Results and discussion:

From TGA thermo grams, various thermal properties such as initial decomposition temperature, the decomposition temperature range and the maximum degradation along with the percentage weight loss of chalcones are reported in Table 2.

For all the compounds of AC series, degradation is multi step process for compounds AC-3 to AC-6. It is evident from Table 2 that the decomposition temperature range for AC compounds is quite wide i.e., between 179-782^{0}C. Generally, thermal stability depends on structure of compounds. In the studied AC compounds, central moiety is same for all the compounds but substitutions are different. The nature and position of these substitutions generally affect thermal properties. AC-2 is found to be most stable whereas A-3 is less stable. This suggests that the presence of nitro group (as in AC-2) causes greater stability than that of chloro group (as in AC-3). Further, % weight loss for these compounds also varies considerably. The % weight loss is maximum for AC-1 containing 4-methoxy group and minimum for AC-5 having no substitution.

In case of NC series, for all the compounds, degradation is single step process. **T**he decomposition temperature ranges for the studied compounds are not very high. The compounds NC-4 and NC-6 are most stable whereas NC-2 is least stable. This suggests that the presence of 4-bromo and 4-hydroxy groups increase the stability whereas 4-nitro group decreases the stability to a greater extent. Further, maximum weight loss is observed for NC-5 and NC-6.

Comparison of thermal stability data of both series shows that in AC series, presence of nitro group increases the stability whereas the same group in NC compound causes decrease of thermal stability. Similarly, % weight loss in AC series is maximum for compound AC-1 containing 4-methoxy group whereas in NC series when there is no substitution (as in NC-5) and when hydroxyl group is present (as in NC-6), maximum loss in weight is observed. This suggests that thermal decomposition depends on structural as well as intermolecular interactions within the compound.

Each step is of different order. Further, 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. However,

Further, from these thermo grams, various kinetic parameters, such as order of the degradation, energy of activation, frequency factor and entropy change have also been evaluated using Anderson-Freeman equation [22]:

$$\Delta \ln dw/dt = n \Delta \ln W - (E/R) \Delta (1/T)$$

Where dw/dt is the rate of decomposition, W is the active mass, R is gas constant and T is temperature. n is order of degradation and E is energy of activation.

The frequency factor (A) and the entropy change (ΔS) were determined by following equations [23]:

$$A = (E\beta/RT^2)\, e^{E/RT}$$

$$\Delta S = R \ln (Ah/kT)$$

Where β is heating rate (10^0C per minute), *h* is Planck's constant and *k* is Boltzmann constant.

The evaluated kinetic parameters are reported in Tables 3 and 4. As reported earlier, for AC, degradation is two step processes whereas for NC compounds, it is single step process.

It is evident from Tables 3 and 4 that order of reaction are quite different in different steps for different chalcones. For AC compounds, order of reaction varies from 1.00 to 6.00 for the first step. Compounds AC1 and AC-2 degrade in single step. For rest of four compounds, variation is from 3.50 to 7.00 in second step. In first step, energy of activation is maximum for AC-6 and minimum for AC-3. The frequency factor and entropy also vary in the same order i.e., maximum for AC-6 and minimum for AC-3. The entropy is negative for AC-3.

In second step, energy of activation, frequency factor and entropy are maximum for AC-6 and minimum for AC-4. Comparison of E and A values of first and second steps show that these values are minimum for second steps of all the chalcones. For the second step, entropy values are found to be negative for all the four chalcones.

For NC compounds, degradation is only a single step process so kinetic parameters are only for first step and are given in Table 3. The order of reaction is minimum for NC-6. However, energy of activation, frequency factor and entropy values are maximum for NC-6. Further, entropy values are negative for NC-1, NC-2, NC-3 and NC-4. The positive values of ΔS indicate that the transition state is less ordered than the original compound whereas negative value of ΔS corresponds to an increase in the order of transition state than the reactants (64).

From DSC, melting points of all the compounds were determined and are given in Table 4 along with melting points determined by open capillary method. It is observed that there is good agreement between the values evaluated from DSC and those determined by open capillary method.

Conclusions:

Thus, the degradation in the studied chalcones varies to a great extent. For some compounds, it is multi step process with different order of reaction. The thermal stability depends upon the structure structural as well as intermolecular interactions within the compound.

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Figure 1: General structure of [A] AC and [B] NC series of chalcones.

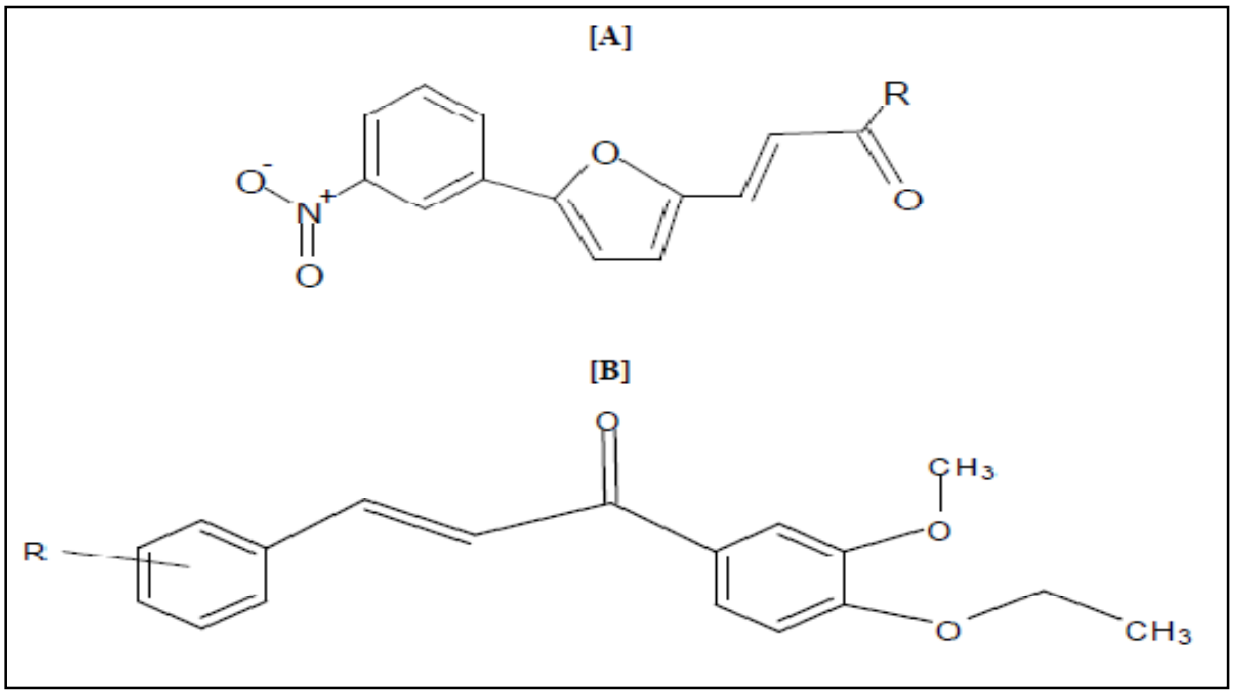

Table 1: Physical constants and substitutions groups of synthesized Chalcones.				
Compd. Code	R	Mol. Wt (g.mol^{-1})	R_f^* value	Yield %
AC-1	4-OCH_3-C_6H_6	349.33	0.48	58
AC-2	4-NO_2-C_6H_6	364.30	0.50	54
AC-3	4-Cl-C_6H_6	353.75	0.42	60
AC-4	4-Br-C_6H_6	398.20	0.48	68
AC-5	--C_6H_6	319.31	0.47	60
AC-6	4-OH-C_6H_6	335.31	0.51	56
NC-1	-4-OCH_3	312	0.68	73
NC-2	-4-NO_2	327	0.58	59
NC-3	4-Cl	316	0.51	73
NC-4	-4-Br	298	0.30	59
NC-5	-H	282	0.49	66
NC-6	-4-OH	469	0.54	85

*Hexane: Ethyl acetate-8:2- For AC Compounds; 0.2:0.8 – Methanol: Chloroform-For NC compounds

Table 2: TGA data for synthesized compounds				
Compound Code	Amount (mg.)	Initial Decomposition Temperature (^{0}C)	Decomposition Range (^{0}C)	% Wt. loss
AC-1	4.545	179	179-325	55.71
AC-2	3.621	210	210-450	53.00
AC-3	4.053	169	169-671	24.80
AC-4	4.413	186	186-706	34.82
AC-5	4.307	176	176-689	20.00
AC-6	4.845	179	179-782	32.40
NC-1	6.375	130	130-500	95.96
NC-2	6.642	80	80-450	55.51
NC-3	6.105	150	150-450	67.41
NC-4	6.115	160	160-496	65.27
NC-5	7.131	150	150-496	93.14
NC-6	7.111	160	160-500	93.14

Table 3: The kinetic parameters of synthesized compounds (I st step decomposition)				
Compound Code	n	E (kJmol^{-1})	A (sec^{-1})	ΔS (J.mol^{-1}.K^{-1})
AC-1	3.20	64.66	1.36×10^{5}	1.35×10^{-3}
AC-2	6.00	381.05	5.01×10^{37}	625.22
AC-3	3.30	35.38	178.43	-53.60
AC-4	3.72	136.58	2.54×10^{12}	140.00
AC-5	1.50	475.08	9.06×10^{45}	783.10
AC-6	1.00	554.26	2.60×10^{55}	964.41
NC-1	2.72	1.74	5.11×10^{-3}	-140.477
NC-2	6.17	16.43	1.43	-93.5315
NC-3	5.09	16.42	1.39	-93.7675
NC-4	4.43	20.49	4.77	-83.4241
NC-5	1.66	150.49	1.32×10^{14}	173.7023
NC-6	1.65	152.27	2.30×10^{14}	179.3199

Table 3: The kinetic parameters of synthesized compounds (II st step decomposition)				
Compound Code	n	E ($kJmol^{-1}$)	A (sec^{-1})	ΔS ($J.mol^{-1}.K^{-1}$)
AC-1	-	-	-	-
AC-2	-	-	-	-
AC-3	5.20	13.93	0.16	-113.90
AC-4	5.30	14.84	1.98	-99.00
AC-5	3.50	24.94	1.52	-95.00
AC-6	7.00	27.71	2.23	-92.00

Table 4: The melting temperatures (^0C) of synthesized compounds by DSC and open capillary methods		
Compound Code	DSC (^0C)	Open capillary method (^0C)
AC-1	142.91	141-143
AC-2	217.83	217-218
AC-3	177.06	175-177
AC-4	158.42	158-160
AC-5	145.53	142-144
AC-6	157.08	156-158
NC-1	151.21	151-152
NC-2	151.92	151-153
NC-3	151	151-153
NC-4	139.01	139-141
NC-5	130.86	130-132
NC-6	130.20	130-132