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# Determination of Thermal Stability and Kinetic Parameters of 1,1'-bis(3-methyl-4-hydroxyphenyl)Cyclohexane by Thermo-Analytical Techniques

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## ABSTRACT

1,1'-bis(3-methyl-4-hydroxyphenyl)cyclohexane (MEBC) was synthesized by acid-catalysed condensation. The structure of compound was supported by $^{1}H$ NMR and $^{13}C$ NMR. The purity and mass of the compound can be confirmed by using a GC-MS analysis. Thermal stability study of compound have been investigated using TG and DSC techniques under $N_2$ at the heating rate of 10 $^{o}C$ $min^{-1}$. Thermal stability and kinetic parameters were determined according to Anderson - Freeman method and discussed.

**KEYWORDS:** Kinetic parameters, Bisphenols, Thermal decomposition, TG, DSC.

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## INTRODUCTION

Bisphenols are widely used for the synthesis of fire resistance polymers and thermally stable bio-molecules[1,2]. The most important terminology for fire resistance polymers and stable bio-molecules is stability against temperature. Thermal stability and degradation mechanism of compounds give valuable information about quality of compounds and also gives an idea whether material need to be reconstructed or not. So that the stability and kinetics of degradation need to be patterned but it is challenging and difficult assignment due to number of variable parameters provide a complex results [3-5]. Numbers of methods are available for determination of thermodynamic and kinetic parameters and but most reliable methods are thermo-analytical methods such as differential scanning calorimetry (DSC), thermogravimetry analysis (TGA) and differential thermal analysis (DTA) etc [6-7]. This techniques are widely used in pharmaceutical and polymer industries to check the quality of material, make possible to determine oxidative chemical reaction and optimum storage conditions[8-9].

In this research work, we studies the thermal stability study and related kinetic parameter of 1,1'-bis(3-methyl-4-hydroxyphenyl) cyclohexane (MEBC) which shows antibacterial, antifungal and antioxidant activity [10-12]. It used as an important constituent in synthesis of polymers[13]. In both of case, studies of thermal stability, decomposition and kinetic parameters are more interested.

## EXPERIMENTAL

## MATERIALS AND MEASUREMENTS

The chemicals and solvents used for a synthesis were of AR grade. $^1$HNMR spectrum was recorded using DMSOas a solvent and TMS as an internal standard on a Brucker Avance III 400 MHz NMR spectrometer. Purity data was recorded on an Agilent GC-7820A and mass spectrum was recorded on an Agilent MS-5977B by using EI (0.7kV) detector. Thermogravimetric analysis (TGA) was carried out on a Shimadzu DTG-60 at the heating rate of 10ºC min$^{-1}$ in $N_2$atmosphere of flow rate 100 ml/min. Differential scanning calorimetric (DSC) measurement was carried out on a Shimadzu DSC 60 at the heating rate of 10ºC min$^{-1}$ in $N_2$ atmosphere of flow rate 100 ml/min.

## SYNTHEIS OF 1,1'-BIS(3-METHYL-4-HYDROXYPHENYL)CYCLO-HEXANE (MEBC)

Cyclohexanone (0.5 mol) was treated with cresol (1.0 mol) in the presence of mixture of HCl: $CH_3COOH$ (2:1 v/v, 100:50 ml) as a Friedel-Craft catalyst at 55$^0$C for 4 h. The pink colored product was filtered, washed well with boiling water and treated with 1N NaOH solution. The resinous

material was removed by filtration through cotton plug. The yellowish solution so obtained was acidified with diluted hydrochloric acid, filtered and dried at 50°C. Compound was crystallized repeatedly from methanol-water systems. The yield of MEBC was ~77% and m. p. was 192°C.

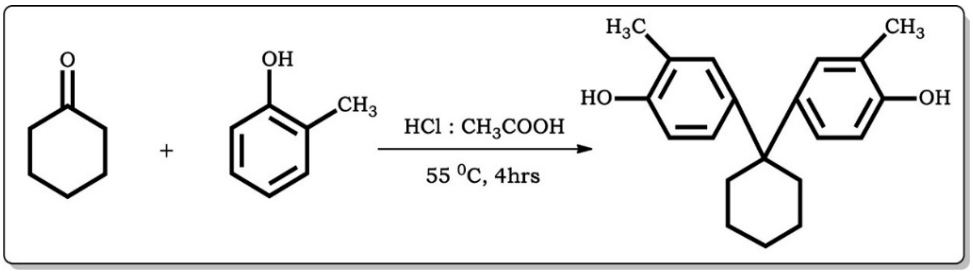


**Figure 1: Reaction scheme of synthesis of 1, 1'-bis(3-methyl-4-hydroxyphenyl)cyclohexane(MEBC)**

## RESULT AND DISCUSSION

## $^1$H NMR ANALYSIS

In MEBC, six protons of cyclohexane ring are observed at 1.434 ppm as a singlet while other four protons are also observed as a singlet at 2.127 ppm. This four protons of cyclohexane rings are overlapped with methyl protons of aromatic ring. Six methyl protons of aromatic ringgives a singlet signal at 2.076 ppm.The sharp singlet at 9.021 ppm was assigned to Ar-OH protons. Resonance of aromatic protons are appeared between6.659-6.948 ppm. DMSO and water peaks appeared at 3.22 and 1.50 ppm as separate peaks. The NMR spectrum of MEBC are shown in Figure 2.

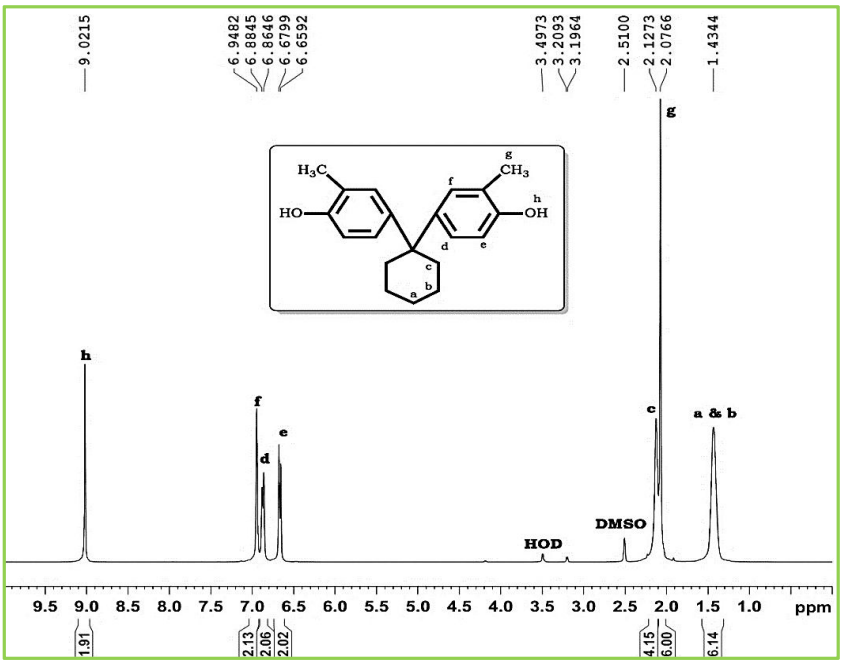


**Figure 2: $^1$H NMR spectrum of MEBC**

## $^{13}$C NMR ANALYSIS

Six non-identical carbons of aromatic rings shows a different signals between 114 to 155 ppm. The carbon atom C5 give arise to small peak than other carbons due to smaller nuclear overhauser effect (NOE).The C8 carbon is most deshielded by oxygen and give a signal at 152 ppm. Cyclohexane ring give a four signals in which C2 and C3 are identical carbons and gives a signals at 22.58 and 36.6 ppm, respectively. The C4 carbon is a quaternary carbon shows peak at 43.36 ppm while C1 shows peak at 25.93 ppm with lower intensity due to least amount of NOE. The methyl carbon (C11) in compound appeared in shielded and gives a signal at 16.39 ppm. DMSO gives a broad signal between 38.78 to 40.03ppm as a septet due to presence of six deuterium atoms. The $^{13}$CNMR spectrum of MEBC is shown in Figure 3.

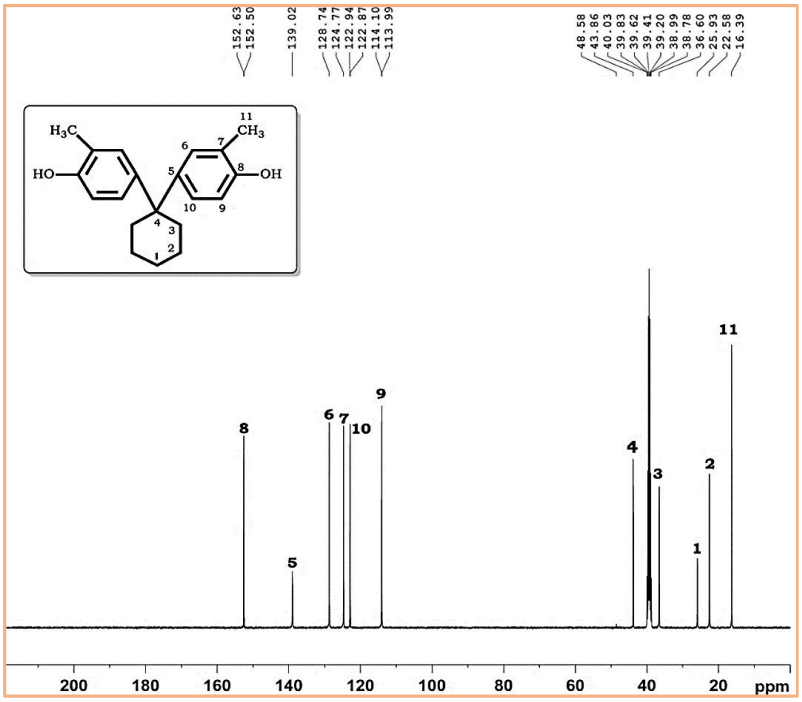


**Figure 3: $^{13}$C NMR spectrum MEBC**

## GC-MS ANALYSIS

Purity data was recorded on an Agilent GC-7820A using HP-1 column and mass spectrum was recorded on an Agilent MS-5977B by using EI (0.7kV) detector. In chromatogram, runtime of eluted peak observed at 20.0 min indicate with 100% area. This indicate that high purity of compound shows in figure 4. The observed m/z value of the compound is 296.2 that is identified from the mass spectrometer library matching shows in Figure 5.

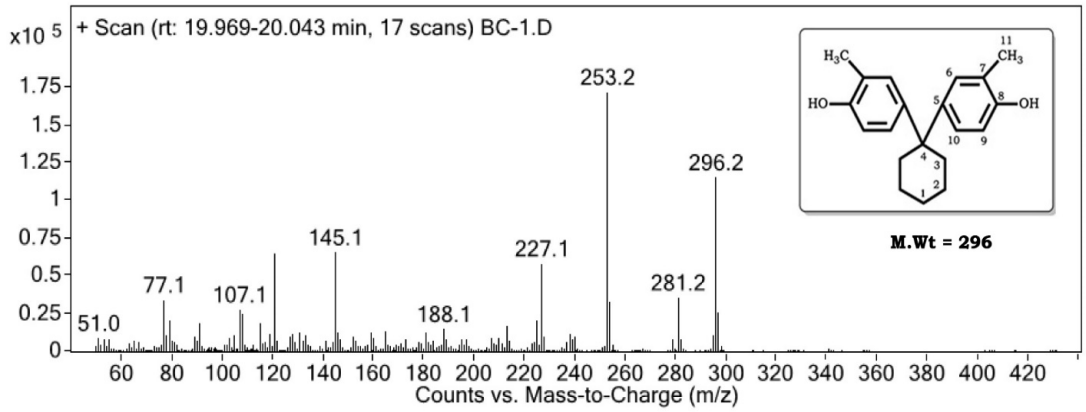


**Figure 4: GC chromatographic peak ofMEBC**

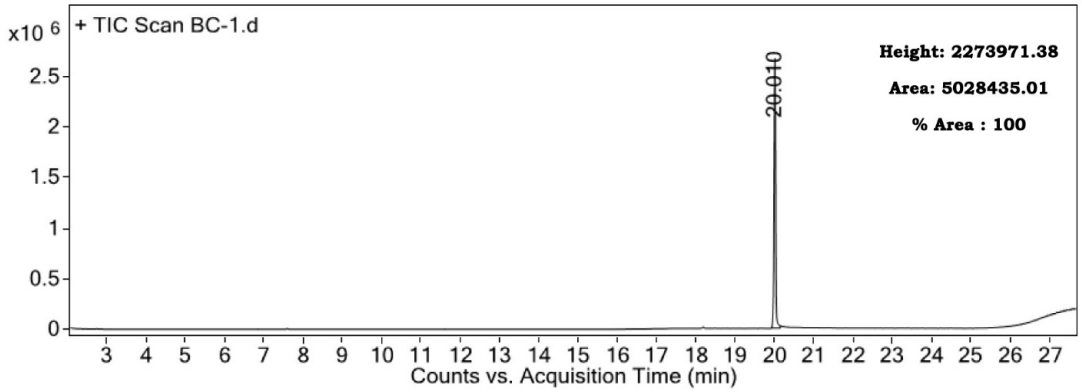


**Figure 5: Mass spectrumof MEBC**

## THERMAL ANALYSIS

DSC thermogram of MEBC at 10ºC $min^{-1}$ heating rate in nitrogen atmosphere is presented in Figure6. The melting transitions ($T_m$) along with heat of fusion ($\Delta H$) and entropy of transitions ($\Delta S$) are listed in Table 1. The sharp endothermic transition at 189.54 ºC (onset) is due to melting of MEBC. Observed heat of melting and entropy are 48.38 $kJmol^{-1}$ and 103.87 $JK^{-1}mol^{-1}$, respectively.

**Table 1. DSC data of 1, 1'-bis(3-methyl-4-hydroxyphenyl)cyclohexane**

| Compounds | Melting transitions, $T_m$ ($^0$C) | Heat of fusion, ΔH (J $g^{-1}$) | ΔH (kJ $mol^{-1}$) | Entropy of transition, ΔS (J $K^{-1}$ $mol^{-1}$) |
|---|---|---|---|---|
| MEBC | 189.54 | 77.73 | 48.38 | 103.87 |

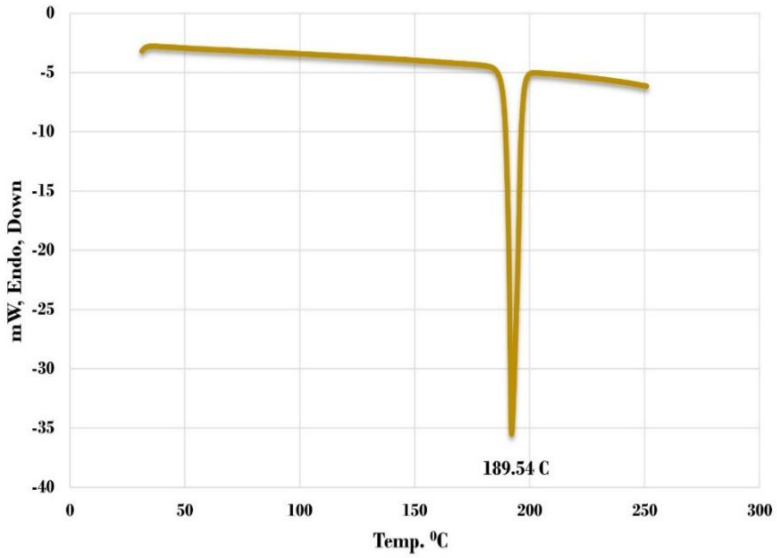


**Figure6. Endothermic transition peak of MEBC at 10°C min$^{-1}$ heating rate under $N_2$ atmosphere**

TGA thermogram of MEBC at 10ºC min$^{-1}$ heating rate in nitrogen atmosphere is presented in Figure 7. Various characteristic temperatures such as initial decomposition temperature ($T_0$), decomposition range, temperature of maximum mass loss ($T_{max}$), % mass loss involved in each step and % residue left at the end of the decomposition reaction are reported in Table 2. MEBC is thermally stable up to about 240 ºC and followed a single step degradation reaction involving 95.05 % weight loss over the temperature range from 240-345 ºC leaving 2.5% residue above 400 ºC. The maximum weight loss was determined from differential thermo gravimetric curve and it is 312 ºC.

| Compounds | $T_0$ (°C) | Decom. Range (°C) | $T_{max}$ (°C) | % mass loss | % Residue at 600 (°C) |
|---|---|---|---|---|---|
| MEBC | 240 | 240-345 | 312 | 95.05 | 2.5 |

**Table 2 TGA data of MEBC**

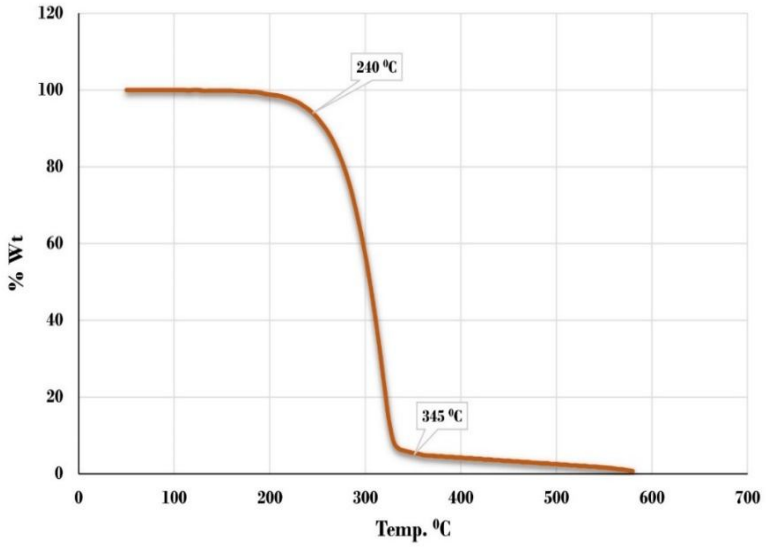


**Figure 7. TGA curve of MEBC at 10°C min$^{-1}$ heating rate under $N_2$ atmosphere**

Associated kinetic parameters such as order of reaction (n), activation energy ($E_\alpha$) and frequency factor (A) were determined according to the Anderson-Freeman method [14-15].

$$\Delta ln\frac{dw}{dt} = n\Delta ln\, w - \left(\frac{Ea}{RT}\right)\Delta\left(\frac{1}{T}\right) \qquad \ldots 1$$

$$A = \frac{Ea\beta}{RT^2}\, e^{Ea/RT} \qquad \ldots 2$$

$$\Delta S^* = R\, ln\, \frac{Ah}{kT} \qquad \ldots 3$$

Where d*w*/d*t* is the rate of decomposition, *w* is the active mass, $\beta$ 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 $E_a$, A, n and regression coefficient $R^2$ are 88.12 kJmol$^{-1}$, 3.73×10$^5$ s$^{-1}$, 0.74 and 0.99, respectively. The entropy change ΔS* was evaluated at 312 °C and it is -143.8. The negative magnitude of ΔS* confirmed that the transition state is in orderly state.

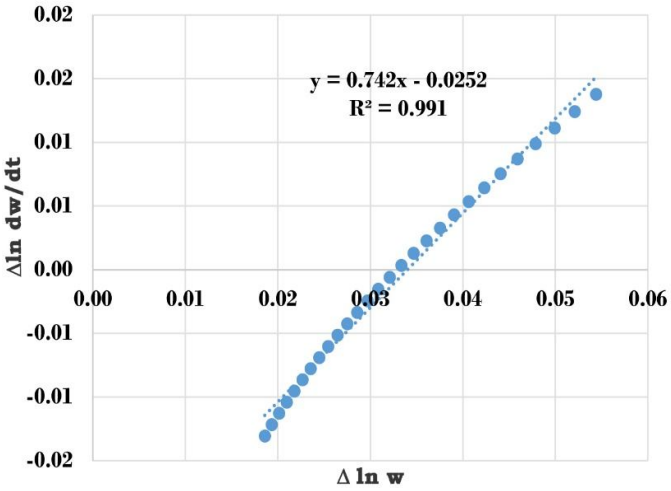


**Figure 8. Anderson-Freeman plot of1, 1'-bis(3-methyl-4-hydroxyphenyl)cyclohexane (MEBC)**

Magnitudes of $E_a$ and $A$ depends on the symmetry and rigidity of the molecules. The value of $E_a$ and $A$ of MEBC shows in below Table 3.

**Table 3 Kinetic parameters of MEBC derived according to Anderson-Freeman method**

| Compounds | n | $E_a$ (kJ mol$^{-1}$) | A ($S^{-1}$) | $\Delta S^*$ (J K$^{-1}$ mol$^{-1}$) | $R^2$ |
|---|---|---|---|---|---|
| MEBC | 0.74 | 88.12 | $3.73\times10^5$ | -143.8 | 0.991 |

## CONCLUSIONS

Spectral data support the structure of 1, 1'-bis(3-methyl-4-hydroxyphenyl)cyclohexane (MEBC). Thermal data revels that compound is stable up to about 240 ºC and followed single step decomposition with fractional order kineticssupporting degradation mechanism.

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