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ORIGINAL ARTICLE

Structural effects and thermal decomposition kinetics of chalcones under non-isothermal conditions

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Abstract Two chalcones namely, 1,5-bis(4-hydroxy-3-methoxyphenyl)pentan-1,4-dien-3-one (BHMPD) and 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (BHMBC) have been synthesised and characterized by microanalysis, FT-IR, mass spectra and NMR (^{1}H and ^{13}C) techniques. The thermal decomposition of these compounds was studied by TGA and DTA under dynamic nitrogen atmosphere at different heating rates of 10, 15 and 20 K min^{-1}. The kinetic parameters were calculated using model-fitting (Coats–Redfern, CR) and model-free methods (Friedman, Kissinger–Akahira–Sunose, KAS and Flynn–Wall–Ozawa, FWO). The decomposition process of BHMPD and BHMBC followed a single step mechanism as evidenced from the data. Existence of compensation effect was noticed for the decomposition of these compounds. Invariant kinetic parameters are consistent with the average values obtained by Friedman and KAS isoconversional method in both compounds.

1. Introduction

Curcumins have several biological activities, such as anti-inflammatory, antioxidative, antibacterial, antihepatotoxic, hypertensive and hypocholesterolemic properties (Chang et al., 2003; Sharma, 1976; Sharma et al., 1972, Gafner et al., 2004; Bennett, 1986). Curcumin inhibits *in vitro* lipid peroxide formation by liver homogenates of endemic mice (Tonnesen, 1986). It is used for the synthesis of bioactive pyrimidine compounds (Das et al., 2006) and also finds applications in the preparation of liquid–crystalline polymers (Gangadhara and Kishore, 1995). Thermotropic liquid crystalline behavior of polymeric materials containing cyclopentanone moiety linked with polyethylene spacers is of considerable current interest, not only because of their potential as high-strength fibers, plastics, moldings, etc. (Griffin and Johnson, 1984; Blumstein, 1985; Chapoy, 1986), but also of their applications in non-linear optical materials (Kawamata et al., 1996). The benzylidene derivatives are intermediates in various pharmaceuticals, agrochemicals and perfumes (Ogawa et al., 1988). Curcumin demonstrated a great ability in chelating essential metal ions such as Cu(II) (John et al., 2002) and the complexes showed a higher scavenging ability than curcumin. The aim of this work is to

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determine the thermal stability and decomposition mechanism of chalcones.

In this paper, we report the synthesis of 1,5-bis(4-hydroxy-3-methoxyphenyl)pentan-1,4-dien-3-one (BHMPD) and 2,5-bis(4-hydroxy-3-methoxybenzylidene)cyclopentanone (BHMBC) and their thermal decomposition in non-isothermal dynamic nitrogen atmosphere condition. The kinetic and thermodynamic parameters are determined using model-fitting and model-free methods.

2. Experimental

2.1. Materials

All the chemicals were of AnalaR grade, purchased from Sd fine chemicals and were used as such without further purifications.

2.2. Instruments

Elemental analyzes were performed on a Carlo Analyzer at Central Drug Research Institute (CDRI), Lucknow, India. FT-IR spectra were recorded in a KBr-pellet on an Avatar-330 spectrometer (with resolution 2 cm^{-1}). The mass spectra were recorded on a JEOL Gcmate, at the Indian Institute of Technology, Chennai, India. The NMR spectra were recorded on a Bruker AMX 400 MHz for ^{1}H and 100 MHz for ^{13}C NMR with TMS as an internal standard at the Indian Institute of Science, Bangalore, India. The simultaneous TGA and DTA curves were obtained with the thermal analysis system model Perkin Elmer TAC 7/DX Thermal Analysis Controller TAC-7. The TG and DTA analyzes of BHMPD and BHMBC were carried out under dynamic nitrogen atmosphere (100 mL min^{-1}), in an alumina crucible with a sample mass around 10 mg with heating rates of 10, 15 and 20 K min^{-1} from 35 to 700 °C. The kinetic parameters E_a and ln A were calculated using Microsoft® Excel Software. The sample temperature, which is controlled by a thermocouple, did not exhibit any systematic deviation from the preset linear temperature program.

2.3. Synthesis of BHMPD

Dry HCl gas was passed through a solution containing vanillin (1 mmol) and acetone (0.5 mmol) in dry methanol. The solution turned dark pink and yellow precipitate was obtained after the addition of water. It was purified by crystallization from methanol medium (m.p. = 99 °C; lit. = 98–99 °C) (Du et al., 2006).

Elemental analysis: Calculated = C, 70.13; H, 5.19. Found = C, 70.48; H, 5.17. FT-IR (KBr disk, cm^{-1}): $\nu_{C=O} = 1667$, $\nu_{C=C} = 1591, 1511$, $\nu_{C-H} = 1428$ and $\nu_{OH} = 3177$. ^{1}H NMR ($CDCl_3$, δ ppm): 3.82 (methoxy proton), 6.94–7.38 (aromatic protons), 7.40, 9.73 (vinyl protons of the α,β-unsaturated arylidene system), 10.26 (phenolic —OH). ^{13}C NMR ($CDCl_3$, δ ppm): 55.46 (methoxy carbon), 110–148 (aromatic carbons and vinyl carbons), 152.97 (C—O carbons of the α,β-unsaturated arylidene system, 190.86 (carbonyl carbon of arylidene keto moiety).

2.4. Synthesis of BHMBC

Vanillin (1 mmol) and cyclopentanone (0.5 mmol) were heated in a water bath (45–50 °C) until a clear solution was obtained, concentrated hydrochloric acid was then added followed by 2 h stirring. After standing overnight, the mixture was treated with cold aqueous acetic acid (1:1) and filtered. The solid material was washed first with cold ethanol, then with hot water and dried in vacuum. The yellow substance was recrystallized from ethanol (m.p. = 212 °C; lit. = 212–214 °C) (Du et al., 2006).

Elemental analysis: Calculated = C, 71.59; H, 6.68. Found: C, 71.23; H, 6.57. FT-IR (KBr disk, cm^{-1}): $\nu_{C=O} = 1667$, $\nu_{C=C} = 1617$, $\nu_{C-H} = 3005$, $\nu_{C=C} = 1519$ and $\nu_{C-H} = 1421$. ^{1}H NMR ($CDCl_3$ and DMSO-d_6, δ ppm): 7.31 (2H, —OH protons), 6.97–6.98 (2H, aromatic hydrogen), 7.52 (2H, —CH═), 3.94 (6H, OCH_3 protons), 2.15–2.17 (4H, —H_2C—CH_2—). ^{13}C NMR ($CDCl_3$, δ ppm): 195.89 (C═O), 148.06–147.32 (CH, C═C, C—O), 113–134.66 (aromatic carbons), 55.77 (OCH_3), 26.32 (CH_2).

3. Theoretical background

3.1. Model fitting method

The integral method of Coats and Redfern has been most successfully used for studying the kinetics of dehydration and decomposition of different solid substances (Horowitz and Metzger, 1963; Coats and Redfern, 1964; Wendlandt, 1974; Sestak, 1984). The kinetic parameters can be derived from modified Coats and Redfern equation:

$$\ln\frac{g(\alpha)}{T^2} = \ln\frac{AR}{\beta E_a}\left(1-\frac{2RT}{E_a}\right) \cong \ln\frac{AR}{\beta E_a} - \frac{E_a}{RT}, \tag{1}$$

where $g(\alpha)$ is an integral form of the conversion function, the expression of which depends on the kinetic model of the occurring reaction. If the correct $g(\alpha)$ function is used, a plot of $\ln[g(\alpha)/T^2]$ against $1/T$ should give a straight line from which the values of the activation energy, E_a and the pre-exponential factor, A can be calculated.

3.2. Model free methods

Friedman method (Friedman, 1963) is a different method and was one of the first isoconversion methods. The logarithm of the non-isothermal rate law:

$$\beta\frac{d\alpha}{dT} = Ae^{\frac{-E_a}{RT}}f(\alpha), \tag{2}$$

gives

$$\ln\left[\beta\frac{d\alpha}{dT}\right] = \ln\left[A_\alpha f(\alpha)\right] - \frac{E_{a,\alpha}}{RT_\alpha}. \tag{3}$$

Flynn–Wall–Ozawa equation (Flynn and Wall, 1966; Ozawa, 1965):

$$\ln\beta = \ln\frac{0.0048AE_a}{g(\alpha)R} - 1.0516\frac{E_a}{RT}, \tag{4}$$

and Kissinger–Akahira–Sunose (KAS) equation (Kissinger, 1957; Akahira and Sunose, 1971):

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\frac{AE_a}{g(\alpha)R} - \frac{E_a}{RT}. \tag{5}$$

The plots of $\ln(\beta d\alpha/dT)$ *Vs* $1/T$ (Eq. (3)), $\ln\beta$ *Vs* $1/T$ (Eq. (4)) and $\ln(\beta/T^2)$ *Vs* $1/T$ (Eq. (5)) have been shown to give the

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