THERMAL DECOMPOSITION KINETICS OF ROSOCYANIN USING NON-ISOCONVERSIONAL METHODS

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The thermogravimetric analysis of rosocyanin has been carried out by non-isothermal thermogravimetric analysis technique. Kinetic and thermodynamic parameters associated with the thermal degradation of rosocyanin have been calculated using Coats-Redfern, Broido, Madhusudanan-Krishnan-Ninanand Freeman-Carroll methods. The kinetic and thermodynamic parameters calculated using these four methods are in good agreement with each other. The order of degradation calculated using Freeman-Carroll method and Coats-Redfern method are 1.5 and 0.9 for first and second stage of degradation respectively. The analysis of thermal degradation data using different solid state reaction models using Coats-Redfern method showed that degradation follows Mampels first order reaction model.

INTRODUCTION

Curcumin isolated from the rhizome of the herb curcuma longa is extensively used as spice, food preservative and coloring material (Alrawaiq *et al.*, 2014). Curcumin and its derivatives have many biological activities like antioxidant activity, anti-HIV activity, antimicrobial activity, anticarcenogenic activity, antimutagenic activity, anticoagulant activity, antiprotazoal activity, antiulcer activity etc (Lee *et al.*, 2013, Moghadamtousi *et al.*, 2014, Maheshwari *et al.*, 2006). However curcumin degrades in water mediated condition especially at high pH (Wang *et al.*, 1997). Many curcumin metal complexes have better stability and biological activity of than the parent. (Borsari *et al.*, 2002, Zhao *et al.*, 2010, Daniel *et al.*, 2004).

Among the different metal complexes of curcumin, the boron complexes of curcumin have attracted extensive attention in analytical and biomedical research. These complexes are highly active against HIV-protease (Sui *et al.*, 1993) and can be used as chemical sensors for cyanide detection (Chaicham *et al.*, 2010). In addition these can be used as near-infrared imaging probes to detect Aβ-plaques in alzheimer's diseases. (Ran *et al.*, 2009)

Tetra coordinate complexes of boron with curcumin are known for many years in the field of analytical chemistry for the determination of boron. During boron complex formation the bright yellow color of curcumin changes to red. This characteristic color change makes this complex as an excellent reagent to determine boron in low concentration (Katherine *et al.*, 2012). In acid medium curcumin reacts with boric acid to form a 2 : 1 curcumin boron

complex, rosocyanin (Figure 1) (Dyrssen *et al.*, 1972). The instability of rosocyanin in hydrated medium limits its application as a boron determining agent in water mediated conditions (Uppstrom *et al.*, 1976).

Tothe best of our knowledge, no systematic investigation has been published concerning the thermal stability studies of rosocyanin. Keeping this in mind, we had purified the commercial curcumin by column chromatographic method and with the separated HPLC pure quality curcumin the rosocyanin complex was prepared and detailed thermal degradation studies were carried out.
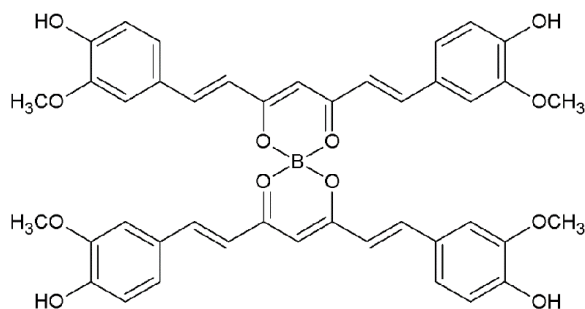

Fig. 1. Structure of rosocyanin.

MATERIALS AND METHODS

The commercial sample of curcumin was purchased from Merck Chemie Pvt. Ltd. Mumbai. Column chromatography using a column packed with **silica gel 60-120 mesh as stationary phase and chloroform as mobile phase were used for the separation of curcumin from commercial sample (Asha *et al.*, 2012).**

UV-Visible spectra were recorded on Elico 198 Biospectrophotometer. Infrared (IR) transmission spectra were recorded at room temperature in a potassium bromide pellet on Perkin Elmer IR spectrophotometer. NMR spectra (^{1}H and ^{13}C) were recorded in DMSO-d_6 on BrukerAvance NMR spectrometer. Thermal gravimetric analyses were recorded on Perkin-Elmer Thermogravimetric Analyzer.

Preparation of Rosocyanin

Rosocyanin was prepared in excellent yield by stirring curcumin (738 mg, 2 mmol) and boric acid (61.8 mg, 1 mmol) in 10 mL toluene and 2 mL con. HCl for 3-5 h at 90-100°C (Sui *et al.*, 1993). The reaction was monitored through TLC and after the completion of the reaction the solvent was removed through filtration to get a dark green powder with metallic luster. The solid product was further purified by washing with toluene to remove unreacted curcumin.

The spectral data of rosocyanin

Yield: 633 mg (85%); UV λ_{max} = 534 nm, ε = 15.11 × 10^4 M^{-1} cm^{-1} (acetone); IR (KBr, cm^{-1}) : 3522 (OH), 1537 (C=O in curcumin), 1284 (C-O in phenol), 1021 (C-O in OCH$_3$); ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.84 (s, 12H, OCH$_3$), 6.77 (s, 2H, CH), 6.90 (d, J = 8.4 Hz, 4H, Ar-H), 7.40 (d, J = 8 Hz, 4H, Ar-H), 8.02 (d, J = 15.6 Hz, 4H, = CH), 7.12 (d, J = 15.6 Hz, 4H, =CH), 7.50 (s, 4H, Ar-H), 10.36 (s, 4H, OH); ^{13}C NMR: δ 55.78, 101.46, 112.91, 116.12, 117.13, 125.97, 148.24, 148.91, 152.32, 176.79; FT-MS, m/z : 745.24 [M$^+$].

Thermal decomposition studies of rosocyanin

The thermal degradation behavior of rosocyanin was evaluated at the heating rate of 10 °C/min from room temperature to 600°C under nitrogen gas flow of 100 mL/min. Kinetic aspects of thermal decomposition were analyzed from the TG-TGA curve; using Coats-Redfern (CR) (Coats *et al*., 1964), Broido (BR) (Broido, 1969), Madhusudanan-Krishnan-Ninan (MKN) (Madhusudanan *et al*., 1986) and Freeman-Carroll methods (Freeman *et al*., 1958).

Data analysis

Data analysis was performed using Microsoft Office Excel worksheet. The goodness of the fit was tested using the correlation coefficient and standard deviation.

RESULTS AND DISCUSSION

The synthesized rosocyanin is characterized by UV, IR, NMR and mass data which corresponds to that reported earlier (Sui *et al*., 1993). The strong C=O stretching frequency of curcumin at 1623 cm^{-1} is shifted to lower wavelength region. A similar reduction in C=O stretching frequency of curcumin was reported for the transition metal complexes of curcumin, where an ionic enol form of curcuminligands to the metals (Priya *et al*., 2015). The broad asymmetric band at 3400–3500cm^{-1}, showed that phenolic groups of curcumin are not involved in condensation reaction which is confirmed by NMR analysis.

Thermal stability studies

Figure 2 shows the TG-DTG curve of rosocyanin. The decomposition stages, determined temperature ranges and corresponding mass losses are given in Table 1. The mass loss in the TG curve is 100% which indicates the complete degradation of rosocyanin. The weight lose below 100°C is due to the evaporation of water molecule. Thermal decomposition of rosocyanin occurs in two stages. The first stage was observed in the temperature range 167-237°C with a mass loss (Calcd./Found %; 25.80, 25.46%) assigned to the loss of substituent groups in the benzene ring. This stage follows a continuous weight loss due to the thermal degradation of remaining part of rosocyanin.
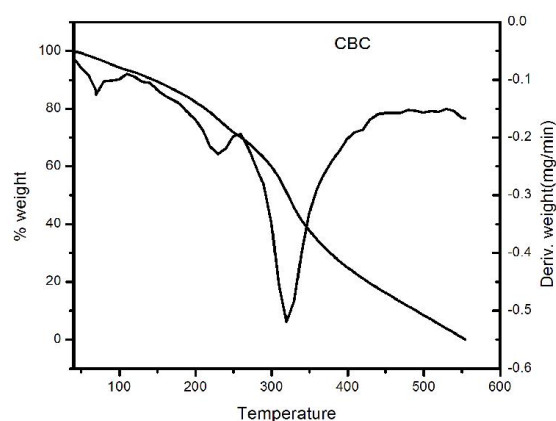

Fig. 2. TG – DTG spectrum for the thermal decomposition of rosocyanin.

Table 1. Thermal decomposition data for rosocyanin.

Stages	DTG	Temperature range	Decomposed assignments	Weight loss (%)
1	227	167-237	4 (OH + OCH$_3$)	25.46
2	317	237-550	Remaining part of rosocyanin	74.54
Residue		Nil		

The best kinetic model which represents the thermal degradation of rosocyanin was studied using CR method. In the present investigation, eleven forms of g(α) have been used to find the most suitable solid state reaction model (Sronsri *et al*., 2015). The form of g(α) which gives better correlation coefficient nearer to one is considered as the mechanism of thermal degradation. The highest value of correlation coefficient is obtained for g(α) = – ln (1 – α) for both stages, which is random nucleation mechanism and this represents Mampel model for first order thermal degradation kinetics. Table 2 lists the eleven form of g(α) and their corresponding R^2 values which were used in this study to determine most suitable kinetic model.

**Table 2. Correlation coefficients obtained for different solid state reaction models.**

Reaction model	g(α)	Correlation coefficient (R^2)	
		First stage	**Second stage**
First order	[– ln (1 – α)]	0.9950	0.9904
Zero order	α	0.9363	0.8883
Second order	[(1 – α)$^{-1}$ – 1]	0.9356	0.8883
Avarami-Erofe'ev (A2)	[– ln (1 – α)]$^{1/2}$	0.9741	0.9720
Avarami-Erofe'ev (A4)	[– ln (1 – α)]$^{1/4}$	0.9471	0.9648
Power law (P2)	α$^{1/2}$	0.9037	0.8708
One dimensional diffusion (D1)	α^2	0.9463	0.8958
Two dimensional diffusion (D2)	[(1– α) ln (1 – α)] + α	0.9615	0.9330
Three dimensional diffusion (D3)	[1 – (1 – α)$^{1/3}$]^2	0.9570	0.9923
Contracting area (R2)	[1 – (1 – α)$^{1/2}$]	0.9741	0.9855
Contracting volume (R3)	[1 – (1 – α)$^{1/3}$]	0.2260	0.9835

CR and FC method were used to calculate the order of thermal decomposition of rosocyanin. The order of thermal decomposition can be determined exactly by using CR method by plotting $ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right]$ vs. 1/T. R^2 value is computed using the least square method for the straight line plots obtained by plotting different values of n ranging from 0 to 2. The n value which gave the best fit value *i.e.*, $R^2 \sim 1$ represents the order of thermal degradation. The data given in Table 3 clearly indicates that the R^2 value nearer to one is obtained for the n value 1.5 for first stage and 0.9 for the second stage and hence these are the orders for thermal degradation. The order can also be calculated from the intercept of FC plot. The value obtained from the FC method is 1.55 and 0.91 respectively for first and second stages. Linear plots (Figure 3a and 3b) obtained for CR, BR, MKN and FC methods also confirmed the first order kinetics for the decomposition process.

Table 3. Calculated R^2 values for different values of n using CR method

Order (n)	R^2	
	Stage 1	**Stage 2**
0.8	0.981371	0.994098
0.9	0.983397	0.995213
1	0.98063	0.994752
1.2	0.987421	0.993797
1.4	0.988414	0.990587
1.5	0.988427	0.988357
1.6	0.988134	0.985747
1.7	0.987552	0.982789
1.8	0.986696	0.979521
2	0.98088	0.972203
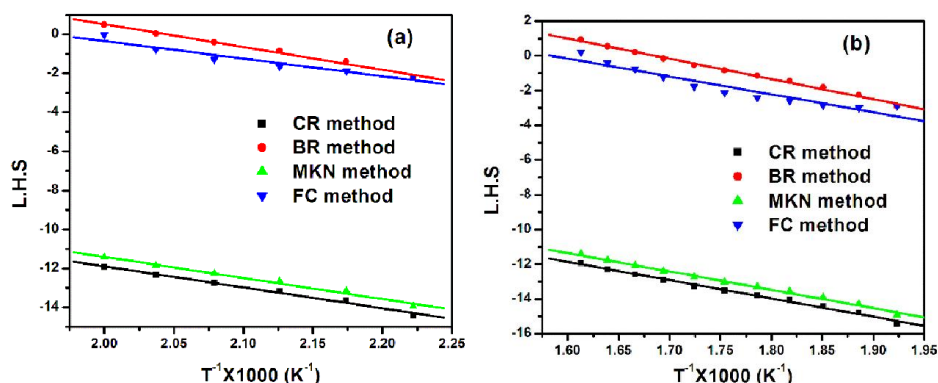
Fig. 3. CR, BR, MKN and FC plot for the thermal degradation of first (a) and second (b) stages.

The kinetic and thermodynamic parameters of the thermal decomposition of rosocyanin *viz.* energy of activation (Ea), frequency factor (A), entropy of activation ($\Delta S^{\#}$), enthalpy of activation ($\Delta H^{\#}$) and free energy of activation ($\Delta G^{\#}$) have been determined for the two degradation stages using CR, BR, MKN and FC methods and the data are given in Table 4. It can be seen that the parameters calculated using these methods are comparable. The high value of Ea revealed the high thermal stability of rosocyanin. The positive value of $\Delta H^{\#}$ means that both stages of decomposition are endothermic in nature. The negative $\Delta S^{\#}$ values indicates more ordered activated state and positive $\Delta G^{\#}$ value means that the decomposition process are non-spontaneous in nature (Sronsri *et al*., 2015).

Table 4. Kinetic parameters of thermal decomposition of rosocyanin calculated using different methods

Stage	Method	R^2	Ea (kJ mol^{-1})	A (s^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
First	CR	0.9879	89.595	2.83×10^7	85.440	− 114.812	142.846
	BR	0.9899	88.840	1.86×10^8	84.683	− 99.186	134.276

	MKN	0.9880	89.861	1.94×10^8	85.704	-98.864	135.136
	FC	0.9884	74.96	4.82×10^7	70.80	-110.42	126.02
	CR	0.9941	87.688	2.66×10^5	82.785	-154.955	174.209
Second	BR	0.9952	94.162	1.96×10^6	89.257	-138.438	170.936
	MKN	0.9941	88.016	1.86×10^6	83.860	-137.512	152.616
	FC	0.9918	85.79	1.27×10^7	80.88	-122.89	153.39

One of the important analogues of rosocyanin is rubrocurcumin and its thermal stability studies were previously reported by the present group (Jeena *et al*., 2016). For the estimation of boron in different matrices presently photometric estimation of rubrocurcumin is more utilized where one of the curcumin present in rosocyanin is replaced by an oxalic acid group. Rubrocurmin provide better colour stability in water mediated reaction condition. The TG analysis of rubro curcumin showed that it is more stable than rosocyanin and have three stage decomposition where oxalate moiety decomposes before the curcumin moiety.The activation energy for the second stage thermal degradation of rubrocurcuminis approximately seven times higher (683.19 kJ mol^{-1}) with a positive entropy of activation (909.54 JK^{-1} mol^{-1}) by CR method (Jeena *et al.*, 2016). The least thermal stability of rosocyanin in comparison with rubrocurcumin may due to its bulky structure.

CONCLUSION

From this study the thermal degradation behaviour of rosocyanin were studied in detail using non-isoconversional methods. The kinetic and thermodynamic parameters calculated using CR, BR, MKN and FC methods were in good agreement with each other indicating the common reaction mode for thermal degradation. The order of reaction calculated using CR and FC methods were in close agreement with each other. The negative value of entropy of activation indicates the activated complex has more ordered structure than the reactant. The best kinetic model that represents the thermal decomposition of rosocyanin was determined using CR method and our result showed that it follows Mampel model for first order thermal degradation kinetics.

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