

# Thermal dehydration and degradation kinetics of chitosan Schiff bases of o- and m- nitrobenzaldehyde

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## Abstract

The thermal dehydration and degradation kinetics of the Schiff bases was studied using different isoconversional methods viz. Kissinger-Akahira-Sunose (KAS), Tang, Starink<sup>1.95</sup>, Starink<sup>1.92</sup>, Flynn-Wall-Ozawa (FWO) and Bosewell from DSC data. The activation energy values of thermal dehydration and degradation reactions obtained from isoconversional methods of FWO and Bosewell are slightly higher than that obtained from other methods. All the isoconversional method yielded consistent values of  $E_a$  for both the dehydration and degradation reactions and is in the order CSB-o < CSB-m.

## 1. Introduction

Chitosan is a linear polysaccharide and the free amino group enable a variety of chemical modifications and substitution processes like carboxyalkylation, acylation, sulfonation, enzymatic substitution, metal chelation, cyanoethylation, nitration, phosphorylation and Schiff's base. The reaction of groups of chitin and chitosan with carbonyl compounds leading to formation of Schiff bases has been reported by several authors (Xu *et al.*, 2003; Lim and Hudson, 2004).

DSC is an ideal tool for rapid screening and finger printing of polymeric materials. The knowledge of the thermal stability and degradation studies of chitosan may help to better understand and plan their industrial processing (Kittur *et al.*, 2002). The objective of the present work is to investigate the kinetics of the thermal

dehydration and degradation of chitosan- Schiff bases formed with o- and m- nitrobenzaldehyde using DSC data, by different isoconversional methods.

## 2. Experimental

The Schiff bases o- and p-nitro benzaldehyde was prepared as reported earlier (Muraleedharan *et al.*, 2017). The DSC experiments were carried out in a Perkin Elmer make (Model: DSC 4000) instrument in the temperature range 303-648 K under an atmosphere of flowing nitrogen. The operational characteristics of the DSC instrument are; flow rate of nitrogen: 20  $\mu\text{L min}^{-1}$ ; sample size: 5 mg and sample pan: aluminium.

### 2.1. Isoconversional Methods

The methods take their origin in the single-step kinetic equation

$$\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right) f(\alpha)$$

(Xu *et al.*, 2003)

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and make use of the isoconversional principle which states that at a constant extent of conversion, the reaction rate is a function only of the temperature so that

$$\left[ \frac{d \ln \left( \frac{d\alpha}{dt} \right)}{dT^{-1}} \right]_{\alpha} = - \frac{E\alpha}{R}$$

(Lim and Hudson, 2004)

In Eqs (1) and (2),  $A$  and  $E$  are Arrhenius parameters (the pre-exponential factor and the activation energy, respectively),  $f(a)$  is the reaction model,  $R$  is the gas constant,  $T$  is the temperature,  $t$  is the time, and  $a$  is the extent of conversion, which can be determined from TG runs as a fractional mass loss or from DSC runs as a fractional heat release. Hence, the subscript  $a$  denotes values related to a constant extent of conversion.

Under non-isothermal conditions, when the temperature is raised at a constant heating rate  $\beta$ , integration of Eq (1) involves solving the temperature integral,  $I(E, T)$

$$g(\alpha) \equiv \frac{A}{\beta} \int_0^{T_x} \left[ \exp \left( \frac{-E}{RT} \right) \right] dt = \frac{A}{\beta} I(E, T)$$

### 3. Result and Discussion

#### 3.1. Dehydration and degradation kinetics

The DSC curves of both Schiff bases obtained at different heating rates are shown in Fig. 1. The values of initial ( $T_i$ ), peak ( $T_m$ ) and final ( $T_f$ ) temperatures for the thermal dehydration and degradation

(Santos *et al.*, 2005)

that does not have any analytical solution. It is solved by using either approximations or numerical integration. All of the approximations lead to a direct isoconversional method in the form:

$$\ln \frac{\beta}{(T^k)} = C - \frac{Ea}{RT}$$

(Kittur *et al.*, 2002)

For each degree of the conversion function,  $a$ , a corresponding  $T_{ai}$  and heating rate are used to plot  $\ln \frac{\beta}{T_{ai}^k}$  against  $1/T_{ai}$ , where  $k$  is a constant. The activation energy is then determined from the regression slope.

The values of activation energy for the thermal dehydration and degradation reactions of these Schiff base derivatives were calculated, using different isoconversional methods like Flynn-Wall-Ozawa (FWO), Kissinger-Aksahira-Sunose (KAS), Tang, Starink and Bosewell, as reported earlier (Muraleedharan *et al.*, 2017).

observed in DSC at different heating rates are given Table 1.

The  $a$ - $T$  data of both the Schiff bases, obtained from DSC, in the range  $a = 0.05$  to  $0.95$  for the thermal dehydration and degradation were subjected to linear least squares analysis using various model-free isoconversional kinetic methods, viz. KAS, Tang, Starink<sup>1.95</sup>, Starink<sup>1.92</sup>, FWO and Bosewell. The activation energy

values were evaluated from the slope of the linear least squares plot. The values of activation energy ( $E_a$ ) obtained from different isoconversional methods through linear least squares analysis of the DSC data for the thermal dehydration and degradation of CSB-o and CSB-m at different conversion is given respectively in Tables 2 and 3.

The linear least squares fit for all isoconversional methods gives good values of regression coefficient. The isoconversional methods of KAS, Tang, Starink<sup>1.95</sup> and Starink<sup>1.92</sup> gave similar values for  $E_a$ , however, the activation energy values obtained from FWO and Bosewell methods are slightly higher than that obtained from other methods. The activation energy

as a function of conversion was plotted and found to vary with conversion, indicating the reaction complexity (not shown). Changes in activation energy during thermal degradation reflect changing mechanism during the reaction.

In the dehydration reaction of CSB-o and CSB-m the  $E_a$  values shows a linear increase with conversion; which is attributed to the initial fast desorption of absorbed gases. It was observed that the values of  $E_a$  increases linearly with conversion for the thermal degradation reaction of CSB-o and CSB-m. All the isoconversional methods yielded consistent values of  $E_a$  for both the dehydration and degradation reactions and is in the order CSB-o < CSB-m.

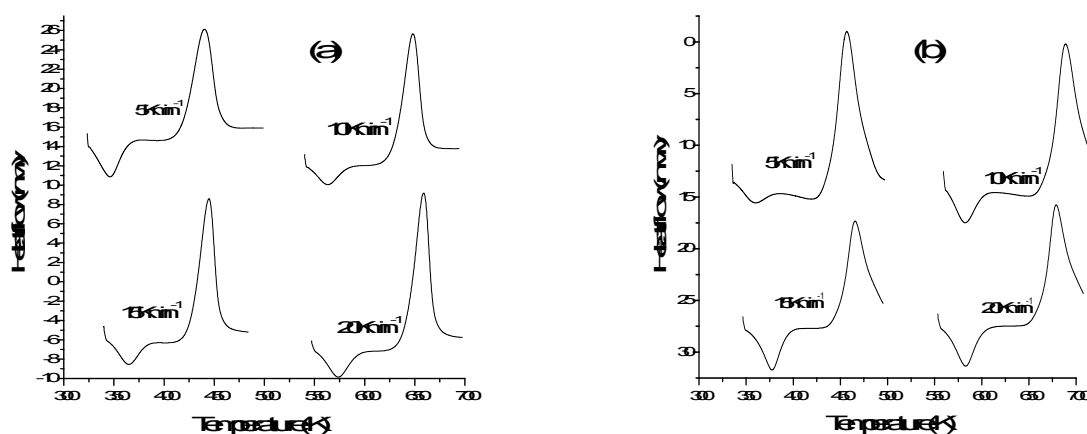


Fig. 1 DSC curves of Schiff bases CSB-o and CSB-m at different heating rates

**Table 1** The initial ( $T_i$ ), peak ( $T_m$ ) and final ( $T_f$ ) temperatures for the thermal dehydration and degradation observed in DSC at different heating rates

Compound	$T / K$	Heating rate / $K \text{ min}^{-1}$							
		Dehydration				Degradation			
		5	10	15	20	5	10	15	20
CSB-o	$T_i$	304	305	308	310	474	472	473	491
	$T_m$	350	354	360	365	532	543	547	552
	$T_f$	398	394	409	415	582	595	605	622
CSB-m	$T_i$	307	307	307	301	488	501	500	517
	$T_m$	356	363	372	366	559	568	574	580
	$T_f$	394	399	431	420	641	646	642	643

**Table 2** The values of activation energy ( $E_a$ ) obtained for the different isoconversional methods through linear least squares analysis of the DSC data for the thermal dehydration and degradation of CSB-o at different conversions.

A	$E_a / kJ \text{ mol}^{-1}$ (Dehydration)					
	KAS	Tang	Starink <sup>1.95</sup>	Starink <sup>1.92</sup>	FWO	Bosewell
0.1	113.7	113.8	113.9	113.9	114.9	115.4
0.2	114.1	114.3	114.5	114.6	115.8	116.4
0.3	115.2	115.3	115.3	115.5	116.5	117.2
0.4	116.2	116.4	116.5	116.6	118.1	118.3
0.5	119.7	119.9	120.1	120.2	120.6	121.8
0.6	124.6	124.8	124.9	125.1	125.8	126.7
0.7	121.7	121.7	121.7	121.8	122.0	122.5



0.8	122.5	122.4	122.5	122.6	123.0	123.2
0.9	123.9	123.9	124.0	124.2	124.8	124.9
Degradation						
0.1	151.0	151.3	151.3	151.2	152.4	152.8
0.2	151.4	151.9	151.8	151.9	152.9	153.6
0.3	151.5	152.3	152.4	152.5	153.2	154.1
0.4	152.2	154.0	154.1	154.1	154.5	156.0
0.5	153.4	154.0	154.6	154.3	155.5	157.9
0.6	158.4	158.5	158.6	158.7	158.9	159.3
0.7	158.4	158.4	158.5	158.6	158.7	159.9
0.8	157.5	157.7	157.8	157.9	158	158.2
0.9	158.1	158.4	158.6	158.8	158.9	159.4

**Table 3** The values of activation energy ( $E_a$ ) obtained for the different isoconversional methods through linear least squares analysis of the DSC data for the thermal dehydration and degradation of CSB-m at different conversions.

$A_9$	$E_a / \text{kJ mol}^{-1}$ (Dehydration)					
	KAS	Tang	Starink <sup>1.95</sup>	Starink <sup>1.92</sup>	FWO	Bosewell
0.1	113.7	113.8	113.9	113.9	114.9	115.4
0.2	114.1	114.3	114.5	114.6	115.8	116.4
0.3	115.2	115.3	115.3	115.5	116.5	117.2
0.4	116.2	116.4	116.5	116.6	118.1	118.3



0.5	119.7	119.9	120.1	120.2	120.6	121.8
0.6	124.6	124.8	124.9	125.1	125.8	126.7
0.7	121.7	121.7	121.7	121.8	122.0	122.5
0.8	122.5	122.4	122.5	122.6	123.0	123.2
0.9	123.9	123.9	124	124.2	124.8	125
Degradation						
0.1	167.8	167.9	167.9	168.2	171.0	171.5
0.2	168.0	168.5	168.6	169.5	171.2	172.8
0.3	169.0	169.5	168.7	169.9	173.1	173.9
0.4	170.5	170.5	171.2	171.3	172.5	176.0
0.5	171.4	171.9	172.4	172.6	174.0	178.2
0.6	176.2	176.9	177.4	178.0	179.0	180.0
0.7	174.2	176.8	177.0	177.7	174.0	178.9
0.8	175.5	175.0	174.8	173.2	176.3	177.5
0.9	175.5	175.0	174.8	173.2	176.3	177.5

#### 4. Conclusion

The activation energy of the thermal dehydration and degradation reactions of Schiff bases CSB-o and CSB-m were investigated by using different isoconversional methods. The results obtained from isoconversional methods show that the values of activation energy for the thermal dehydration and degradation reactions are dependent on conversion. Both the

Thermal dehydration and degradation shows an increase in activation energy with conversion. All the isoconversional methods yielded consistent values of  $E_a$  for both the dehydration and degradation reactions and is in the order CSB-o < CSB-m. It can be concluded that the complexity of the reaction can be identified only through isoconversional methods.

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