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Thermochimica Acta 324 (1998) 25–32

thermochimica
acta

A simultaneous TG-DTA study of the degradation in nitrogen of cellulose to carbon, alone and in the presence of other pharmaceutical excipients

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Abstract

The heat treatment of an α -cellulose and a microcrystalline cellulose (Avicel[®]) in nitrogen gives a one-stage degradation to carbon. This degradation suffers a temperature transposition in the presence of pharmaceutical excipients, namely dibasic calcium phosphate, stearic acid, magnesium stearate, and silicon dioxide. It is possible to produce a kinetic evaluation of these thermal analysis studies in terms of a comparative method by constructing the theoretical TG trace of the binary mixture based on a presumed no-interaction between the two components. There is a variation in behavior to be noted in the different forms of cellulose, and also different values are shown for the Arrhenius parameters. Such variations are also noted in the Avicel[®] degradation in the presence of other materials. These observations should be of use in the characterization of pharmaceutical excipients. The Arrhenius parameters for α -cellulose degradation using D3 (three-dimensional diffusion) mechanism at the temperature range from 580 to 630 K are $289.32 \text{ kJ mol}^{-1}$ and 1.85×10^{23} for E_{act} and A , respectively. The Arrhenius parameters for Avicel[®] degradation using F1 (first-order) mechanism at the temperature range from 562 to 604 K are $291.35 \text{ kJ mol}^{-1}$ and 1.26×10^{25} for E_{act} and A , respectively. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Cellulose; TG-DTA; Dibasic calcium phosphate; Stearic acid; Magnesium stearate; Silica

1. Introduction

In typical pharmaceutical formulations, Avicel[®] finds a use as an excipient because it fills a dual role of binder and disintegrant. However, such an excipient is not used by itself and in typical formulations would exist in the presence of other excipients such as dibasic calcium phosphate, stearic acid, magnesium stearate, and silicon dioxide. In the present study, the thermal behavior in the simultaneous TG-DTA equipment of binary mixtures of Avicel[®] with the above excipients is examined. In addition, it should be noted that the Avicel[®] is really an α -cellulose in which the fibrous nature of the original α -cellulose has been eliminated

by various processing treatments. Accordingly, the behavior of Avicel[®] is compared with an α -cellulose in which the fibrous nature of the native cellulose is retained. The production of the α -cellulose from native cellulose is by way of mercerization treatment of the native cellulose with alkali hydroxides or other alkali metal salts. In this treatment, the cellulose swells and produces the α -cellulose form. The extent and subsequent nature of the processing then determines the amount of the amorphous form, the extent of crystallization, and loss of the fibrous character. It is, of course, possible to study the behavior of these celluloses in air but their combustion either alone or in the binary mixture give a completely different thermal analysis result. Therefore, the present study is confined to reporting the thermal analysis behavior of the celluloses and their binary mixtures with other pharmaceutical excipients in nitrogen.

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2. Material and methods

2.1. Materials

The materials studied were: microcrystalline cellulose (Avicel[®] PH 101, lot # 1401) obtained from FMC Corporation, α -cellulose (lot # 100H0747) and dibasic calcium phosphate, anhydrous (log # 53H0948) purchased from Sigma, stearic acid (lot # 002680) obtained from Sherman Research Laboratories, magnesium stearate (lot # 742748), purchased from Fisher Scientific, and colloidal silicon dioxide (Cab-O-Sil[®] grade M5, lot # 1E252) received from Cabot Corporation. In the case of stearic acid and magnesium stearate, these are really mixtures of stearic acid with palmitic acid and of magnesium stearate with magnesium palmitate.

2.2. Equipment

The thermal analysis equipment used was TA Instrument, simultaneous TG-DTA 2960, with the thermal analyst 2000 TA operating system version 1.0 B software.

2.3. Procedure

Experiments for rising temperatures at the heating rate of $10^{\circ}\text{C min}^{-1}$ in a nitrogen flow of 50 ml min^{-1} were carried out for all the runs in the present study. Alumina crucibles of $90\ \mu\text{l}$ volume were used and the reference crucible was left empty. The amount of material used was varied, depending on their density, to occupy one-half the volume of the container. In order to maximize the effect of the excipient on the Avicel[®] thermal behavior, the binary mixtures of 50 : 50% by mass were prepared. The materials were mixed in a porcelain mortar. The lower density material was placed first in the mortar and an equal amount of the material of higher density was added and blended well.

3. Results and discussion

The TG and DTG plot for α -cellulose is shown in Fig. 1. Details on TG and DTG signals for the degradation of α -cellulose and Avicel[®] are noted in Table 1. The single-stage degradation is due to a complex sequence of reactions and the material

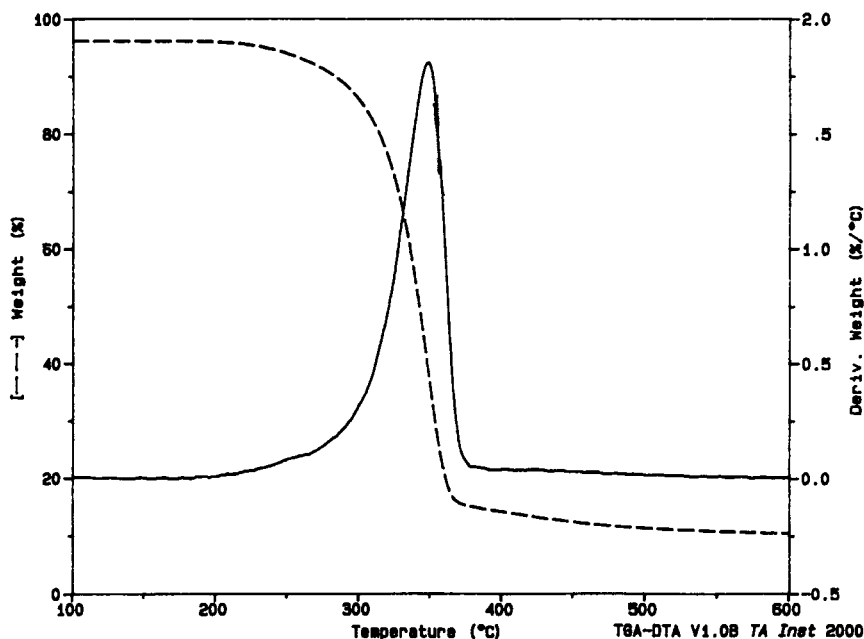


Fig. 1. The TG and DTG plot for α -cellulose at the heating rate of $10^{\circ}\text{C min}^{-1}$ under an atmosphere of dry nitrogen.

Table 1
Details on TG and DTG signals for the degradation of α -cellulose and Avicel[®]

Material	Initial temperature/ $^{\circ}$ C	Final temperature/ $^{\circ}$ C	DTG peak temperature/ $^{\circ}$ C	
α -Cellulose	216.0	542.7	349.0	14.48
Avicel [®]	276.1	542.0	330.8	13.87

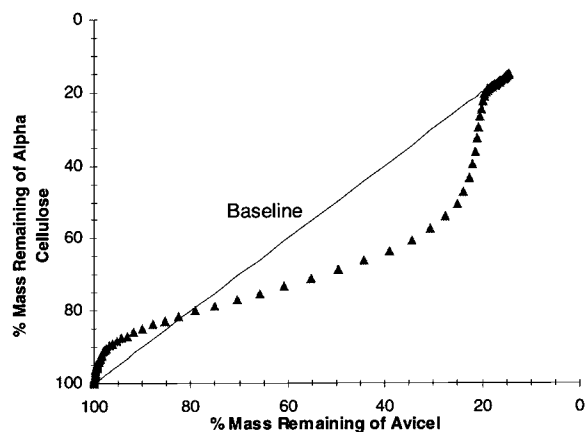


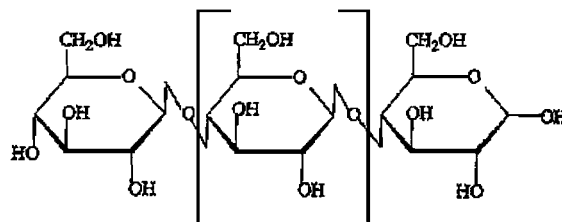
Fig. 2. The plot of % mass remaining at equivalent temperature for α -cellulose and Avicel[®].

remains in the solid state. An examination of these plots suggests the possible mechanisms [1] and the Arrhenius parameters can be calculated [2]. Typical activation energy [3] for α -cellulose (at the fraction decomposed, α , =0.5) is equal to 294.42 kJ mol⁻¹. It is, of course, possible to establish the behavior of the binary mixtures in the same manner. However, it is easy to demonstrate the differences by noting the alteration of the TG curve in the region where the cellulose degrades.

The plot of % mass remaining at equivalent temperature for α -cellulose and Avicel[®] is shown in Fig. 2. This type of plot allows one to compare and contrast the kinetic behavior of the two celluloses on a comparative basis. The degradation of cellulose to the end product of carbon is an endothermic event. This can also be seen as a perturbation on the plot of time vs. temperature and its first derivative (dT/dt) for Avicel[®], as an example in Fig. 3.

In general, any polymer degradation is affected by the chemical nature of its components (the monomeric 'building blocks'), by the temperature, the surrounding atmosphere and the geometry of the crucible in

which the sample is treated [4]. Specifically in the degradation of cellulose, the structure must be noted. Cotton cellulose is a pure glucose polysaccharide (C₆H₁₀O₅)_n, containing <0.05% ash. α -Cellulose is cotton cellulose which has been treated with cold NaOH and is the form generally used for industrial purposes [5]. The D-glucose unit of the polymeric cellulose chain is shown below:



Avicel[®] is a non-fibrous form of cellulose. It was produced by acidolysis of cellulose raw material to remove an amorphous form yielding crystalline material [6]. Differences in properties are due to the fact that α -cellulose is a fibrous form, but the Avicel[®] is a crystalline form [7].

The degradation of cellulose is composed of a set of concurrent and consecutive reactions. The general scheme of this degradation is shown in Fig. 4 [8,9]. It can be seen that levoglucosan [10] occupies a significant position in the general degradation scheme. Its presence in this study goes undetected because only the breakdown products, C, CO, CO₂, H₂O, and combustible volatiles are detected. These combustible volatiles and the carbon are oxidized in air in two stages represented as flaming combustion and glowing combustion, respectively. The process of combustion converts an endothermic degradation into an overall exothermic process.

The mechanism of degradation is a subject of debate. Three commonly quoted initial steps are:

1. the formation of levoglucosan via 1,2-anhydro intermediate [11,12];

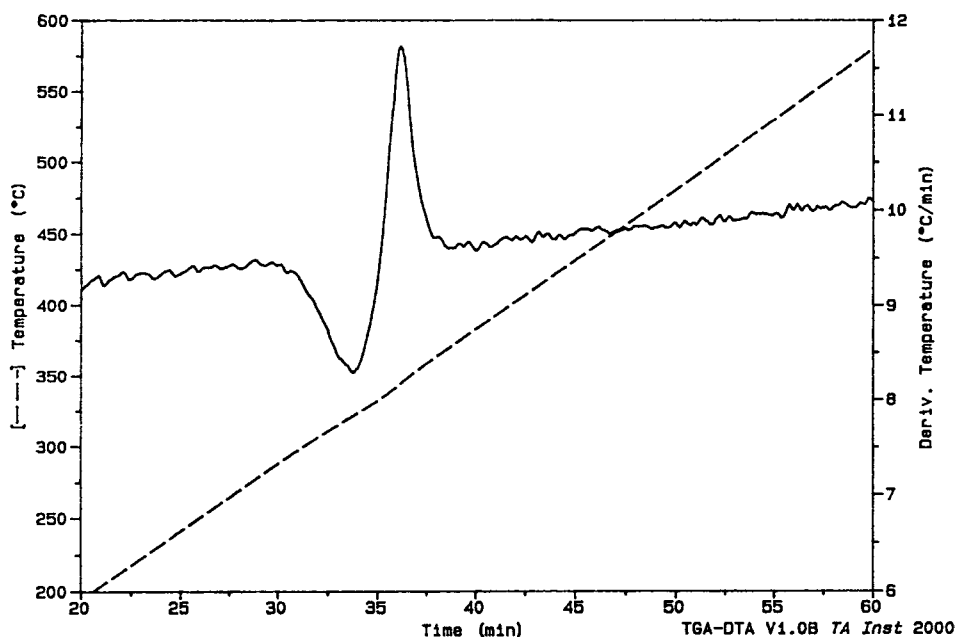


Fig. 3. The plot of time-temperature and its first derivative (dT/dt) for Avicel[®] showing a perturbation at the degradation region.

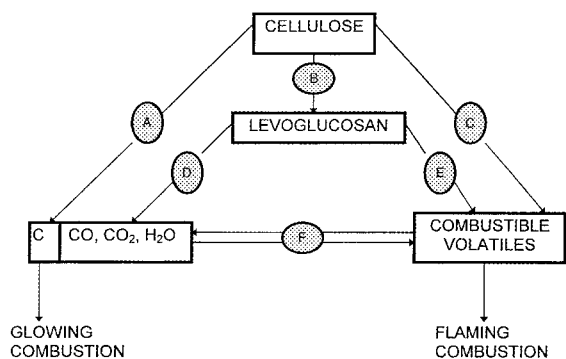


Fig. 4. Thermal degradation of cellulose: pathways labeled A, B and C are termed primary whilst D, E, and F are termed secondary.

2. transglycosylation [9–11,13–16]; and
3. free radical mechanism [12].

However, nobody discusses the breakdown of these degradation compounds, into the end product carbon, via a solid-state reaction. This must be different from the breakdown of simple organic compounds into carbon black which occurs from a gaseous state.

The degradation process would seem at first to be so complex that a kinetic explanation is impossible. However, the experimental data of the breakdown in nitrogen to carbon is seen to be a simple one-stage process. This suggests that a reaction interface exists and processes taking place at this interface are rate controlling. The kinetic interpretation can be considered then as a phase-boundary process. It is shown here, and elsewhere [17,18], that although the overall single-state degradation is retained, the Arrhenius parameters can be altered by the presence of additives [19,20].

In previous publication [3], it was shown that a three-dimensional diffusion (D3) mechanism best described the kinetics for α -cellulose degradation while a first-order (F1) mechanism described that for Avicel[®]. The differences in reaction mechanism lead to the data shown in Fig. 2. This shows clearly the greater reactivity of the α -cellulose at lower temperatures and the greater reactivity of Avicel[®] at higher temperatures. This is due largely to the different kinetic mechanisms. The differential approach is used here:

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

and

$$k = \frac{(d\alpha/dT)\beta}{f(\alpha)} \quad (2)$$

for α -cellulose using D3 mechanism

$$f(\alpha) = 1.5[1 - (1 - \alpha)^{1/3}]^{-1}(1 - \alpha)^{2/3} \quad (3)$$

for Avicel[®] using F1 mechanism

$$f(\alpha) = 1 - \alpha \quad (4)$$

It is then possible to plot $\ln k$ vs. $1/T$ according to the Arrhenius equation

$$\ln k = \ln A - \frac{E_{\text{act}}}{RT} \quad (5)$$

where α represents the fraction decomposed, $f(\alpha)$ the function α , k the kinetic rate constant, t the time in min, T the temperature in K, β the heating rate in K min^{-1} , A the pre-exponential parameter, E_{act} the activation energy, and R the molar gas constant. This leads to the kinetic parameters for α -cellulose and Avicel[®] degradation as follow:

Material (Mechanism)	$E_{\text{act}}/\text{kJ mol}^{-1}$	A	T/K
α -Cellulose (D3)	289.32	185×10^{23}	580–630
Avicel [®] (F1)	291.35	1.26×10^{25}	562–604

and this is sufficient to account for the differences observed in the degradation process as seen in Fig. 2.

The TG curve for the binary mixture of dibasic calcium phosphate with Avicel[®] is shown in Fig. 5 together with a theoretical curve which is constructed by combining the TG signal of the individual substances of the mixture and then dividing by two. This theoretical curve is based on no-interaction between the two components. It can be seen that the fit is almost perfect leading to the conclusion that the Arrhenius parameters for Avicel[®] are retained in this particular binary mixture.

The TG signal for the binary mixture of stearic acid with Avicel[®] is shown in Fig. 6. The theoretical curve, constructed on the same basis of no-interaction of the two components shows a shift for the experimental curve for stearic acid evaporation to a lower temperature but the curves for the degradation of the Avicel[®] coincide. Again, it may be concluded that the kinetic parameters for Avicel[®] are unaltered.

However, the TG plot for the binary mixture of magnesium stearate and Avicel[®] shows large differences between the experimental curve and that calculated for a 50 : 50% binary mixture based on no-interaction between the components as shown in Fig. 7. This is not just due to the fact that the temperatures of decomposition for the two components

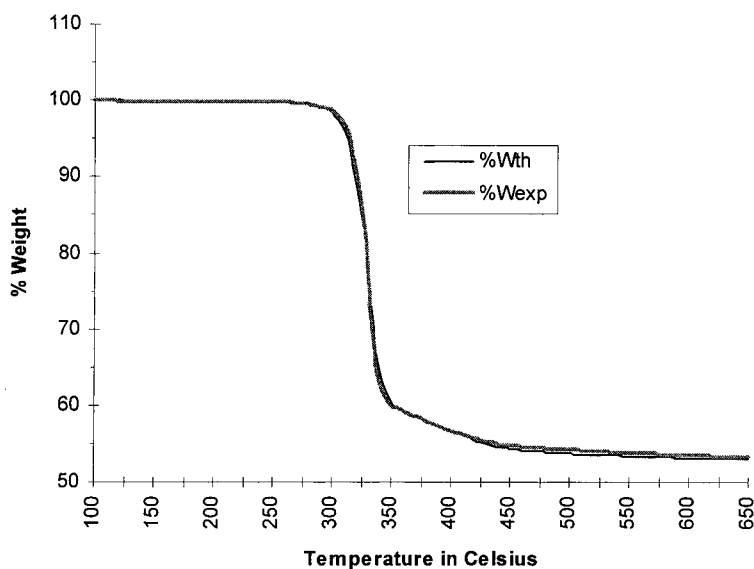


Fig. 5. Comparison of the theoretical and experimental TG curves for the binary mixture of dibasic calcium phosphate with Avicel[®].

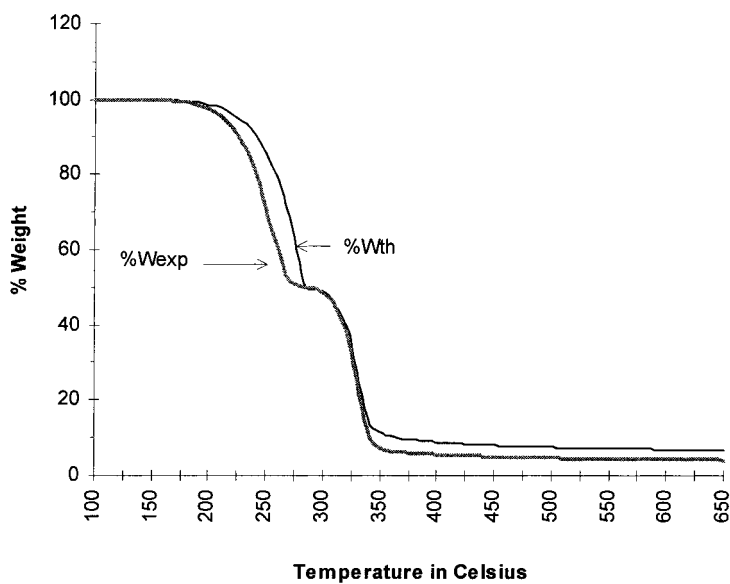


Fig. 6. Comparison of the theoretical and experimental TG curves for the binary mixture of stearic acid with Avicel[®].

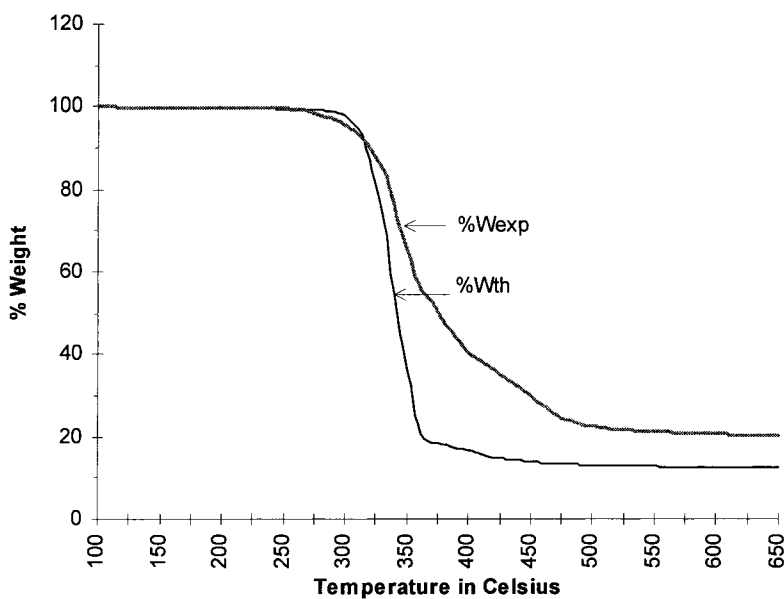
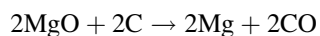


Fig. 7. Comparison of the theoretical and experimental TG curves for the binary mixture of magnesium stearate with Avicel[®].

coincide but must be due to some interaction between the components and/or their reaction products. The end product of magnesium stearate decomposition is MgO together with other carbonaceous products [21]. The end product of Avicel[®] degradation is carbon.

The possibility of the process



occurring cannot be overlooked, but Ellingham free-energy [22,23] considerations would indicate a

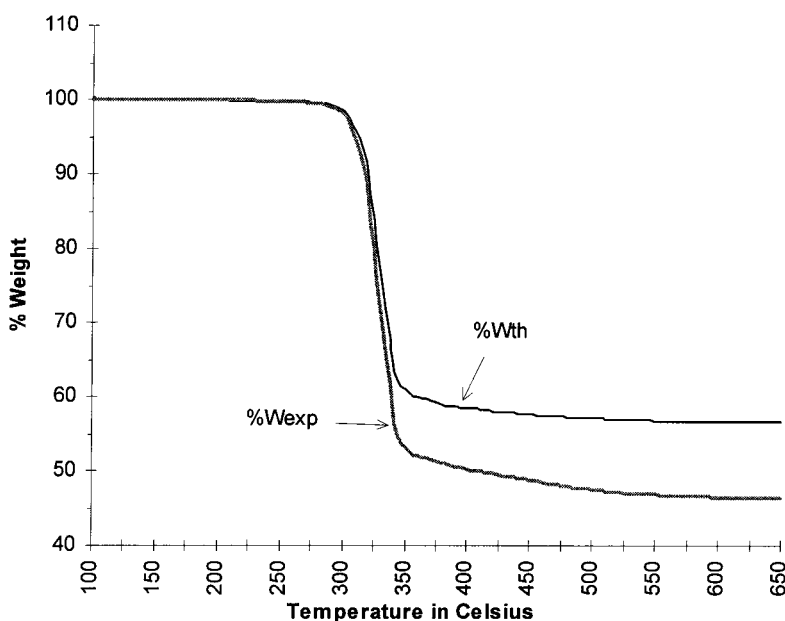


Fig. 8. Comparison of the theoretical and experimental TG curves for the binary mixture of colloidal silicon dioxide with Avicel[®].

high-temperature process. Any reaction is probably confined to a surface interaction. In these circumstances, it is impossible to calculate the kinetic parameters for this binary mixture.

The influence of colloidal silicon dioxide on the degradation of Avicel[®] is seen in Fig. 8. Again, there is coincidence of the experimental Avicel[®] TG trace and the theoretical TG curve and it must be concluded that the kinetic parameters remain unaltered. The difference in the experimental % mass loss between the theoretical and the experimental TG curves can be attributed to the difficulty of making up a perfectly 50% mixture.

4. Conclusion

It is shown that α -cellulose and Avicel[®] differ in kinetic reaction parameters. In binary mixtures of Avicel[®] with dibasic calcium phosphate, stearic acid, and silicon dioxide, the kinetic parameters for Avicel[®] remain unchanged. However, there is an interaction between magnesium stearate and Avicel[®] which is partly due to the correspondence of the degradation processes and partly to the probability of interaction between the solid residue. The Arrhe-

nius parameters for α -cellulose degradation using D3 mechanism at the temperature range from 580 to 630 K are $289.32 \text{ kJ mol}^{-1}$ and 1.85×10^{23} for E_{act} and A , respectively. The Arrhenius parameters for Avicel[®] degradation using F1 mechanism at the temperature range from 562 to 604 K are $291.35 \text{ kJ mol}^{-1}$ and 1.26×10^{25} for E_{act} and A , respectively.

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