KINETIC PARAMETERS OF THERMAL DECOMPOSITION OF COMPLEX OF β-CYCLODEXTRIN WITH WATER

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The apparent kinetic parameters of the thermal decomposition of the β-cyclodextrin-water complex were estimated from thermogravimetric data. Various calculation methods were used and the results compared. All methods except the Kissinger method gave a reaction order near to zero and an activation energy in the range 60 to 65 kJ/mol. Some trials were made to extrapolate the activation energy values to semi-isothermal conditions (65.7 kJ/mol). The loss in weight indicated the presence of 11 water molecules in the complex. This was liberated in single stage, despite its occurrence as two distinct types, as shown by crystallographic studies.

The cyclodextrins are the cyclic oligosaccharides composed of 6, 7 or 8 *D*-glucose residues for *α*, *β* and *γ*-cyclodextrin, respectively. Their structure involves a cyclindrical cavity capable of including various guest molecules to form host-guest inclusion complexes in the solid state and in solution [1]. This complex formation is regarded as an analogue of many phenomena, e.g. Michaelis-complex formation in enzymatic reactions [2–4], and is widely studied as a model system of biological interest [5]. Information about the compositions of the complexes and the dynamic properties of the guest molecules is of fundamental importance for an understanding of the nature of the inclusion complexes. The driving force for complex formation is the removal of high-energy water molecules by guest molecules from the cavity, and the London dispersion interactions [6–8].

This paper describes the thermal decomposition of the β-cyclodextrin—water complex as a preliminary investigation for studies of the physical intermolecular interactions inside the host-guest complexes of the cyclodextrins.

Experimental

Commercially available β-cyclodextrin (Aldrich, Belgium) was recrystallized from distilled water before the experiments.

A derivatograph (MOM, Budapest, Hungary) was used for the thermal decomposition studies, in which 50 mg samples were run against standard of 50 mg of α-Al_2O_3. A platinum semimicro crucible was used for the thermogravimetry. Linear temperature programmings of 0.96, 1.95, 2.97, 4.71, 8.48 and 13.7 deg/min were used. The linear regression method was employed for calculations.

Results and discussion

Figure 1 presents typical thermal analysis curves of the β-cyclodextrin–water inclusion complex. The low-temperature peak between 50° and 110° in the DTG curve corresponds to the loss of water molecules, which escape in one step from the complex. This occurs as an endothermic process with a negative peak in the DTA curve.

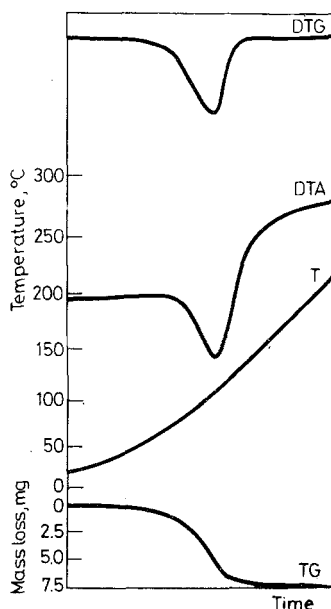Let us assume that, a complex X decomposes into two components, gaseous Y

Fig. 1 Thermal curves of the β-cyclodextrin–water complex. Average heating rate $\varphi = 8.48$ deg/min

and solid Z:

$$aX \xrightarrow[\text{temp.}]{} bY + cZ \tag{1}$$

The kinetics of this can be described by

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \tag{2}$$

where α = fractional conversion, and
    $k(T)$ = rate constant, which can be expressed by the Arrhenius relation:
    $k = A \cdot \exp(-E/RT)$ \hfill (3)
where A = frequency factor,
    E = activation energy,
    R = gas constant, and
    T = absolute temperature.

Function $f(\alpha)$ in (2) is generally described [9] by

$$f(\alpha) = (1-\alpha)^n \alpha^m [-\ln(1-\alpha)]^P \tag{4}$$

where n, m and P are constants.

Equations (2) to (4) have been used in several theories to determine the kinetic parameters of thermal decomposition of complex X from non-isothermal thermogravimetric data obtained at constant heating rate $\Phi = \dfrac{dT}{dt}$.

For estimation of the activation energy, order of reaction and frequency factor of dehydration of the β-cyclodextrin inclusion complex, the published methods [10–16] were applied.

Kissinger [10] has assumed that the temperature of maximal reaction rate, T_m, and the temperature at the maximum of the DTA curve are the same. For the temperature $T = T_m$, where $\dfrac{d}{dt}\left(\dfrac{d\alpha}{dt}\right) = 0$, assuming $f(\alpha) = (1-\alpha)^n$ and $E \gg 2RT$, Kissinger obtained the equation

$$\frac{E\Phi}{RT_m^2} = A \cdot e^{-E/RT_m} \tag{5}$$

which no longer includes the reaction order n. From the logarithmic form of this equation, the activation energy E of thermal decomposition of the β-cyclodextrin complex with water was determined as 72.5 ± 0.8 kJ/mol. In turn, frequency factor A was found to be $\ln A = 18.04 \pm 9.30$ s^{-1}. A similar value of the frequency factor, $\ln A = 18.6 \pm 13.35$ s^{-1}, was obtained from the method of Wendlandt [11].

Since Eq. (5) does not relate the experimental results to reaction order n, Kissinger [10] examined a relation between the reaction order and the shape of the peak of the DTA curve. With decreasing reaction order n, the DTA curve becomes more asymmetrical. Thus, he linked the shape factor S of a peak [10] with the reaction order n by

$$S = 0.63 \, n^2 \qquad (6)$$

Six DTA curves for the cyclodextrin complex showed that the shape factor S was almost independent of the heating rate Φ. The average order of reaction found in this way was $n = 0.78 \pm 0.03$.

Piloyan et al. [12] utilized Borchardt's equation [13] for the initial stages of the reaction, when

$$\Delta T = F \frac{d\alpha}{dt} \qquad (7)$$

where ΔT = the deviation from the baseline of the DTA curve, and

F = the area of the thermal effect, $F = \int\limits_{t}^{\infty} \Delta T \, dt$.

They obtained the following relation [12])

$$\ln \Delta T = C - \ln f(\alpha) - \frac{E}{RT} \qquad (8)$$

where C = a constant.

The term $\ln f(\alpha)$ was finally neglected, providing a simple equation:

$$\ln \Delta T = C - \frac{E}{RT} \qquad (9)$$

For ΔT values at different temperatures between the beginning and the minimum of the DTA curve for the cyclodextrin-water complex (i.e. for a reaction degree of 5–65%), an activation energy $E = 59.1 \pm 0.9$ kJ/mol was calculated for the heating rate $\varphi = 13.7$ deg/min. However, heating rates below 10 deg/min provided higher activation energies, indicating that the validity of neglect of the term $\ln f(\alpha)$ is correct only at high heating rates.

Freeman and Carroll [14] assumed $f(\alpha) = (1-\alpha)^n$ and, using Eqs (2) and (3), obtained the relation

$$\frac{\log \Delta \dfrac{dw_t}{dt}}{\Delta \log W_r} = \frac{\dfrac{E}{-2.3R} \Delta \dfrac{1}{T}}{\Delta \log W_r} + n \qquad (10)$$

where $W_r = W_\infty - W_t$,

W_∞ = loss in weight at completion of reaction, and

W_t = total loss in weight up to time t.

This equation allows simultaneous determination of the activation energy and reaction order n from thermogravimetric curves.

When the thermogravimetric curves of the cyclodextrin-water complex were used for the calculations, no difference in activation energy for different heating rates was observed, although the experimental error increased for faster runs. Figure 2 shows two chosen plots for heating rates:

a) $\varphi = 2.97$ deg/min, $E = 62.4 \pm 0.8$ kJ/mol, and

b) $\varphi = 8.48$ deg/min, $E = 60.2 \pm 1.6$ kJ/mol. Thus, a weighted average value of the activation energy is $E = 61.5 \pm 3.1$ kJ/mol.

The method of Coats and Redfern [15, 16] offers a possibility to determine the activation energy from TG curves. Assuming $f(\alpha) = (1-\alpha)^n$ for a differential equation

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\varphi} \int_0^T e^{-\frac{E}{RT}} dT \tag{11}$$

they obtained

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{\varphi E}\left[1 - \frac{2RT}{E}\right] - \frac{E}{2.3RT} \tag{12}$$
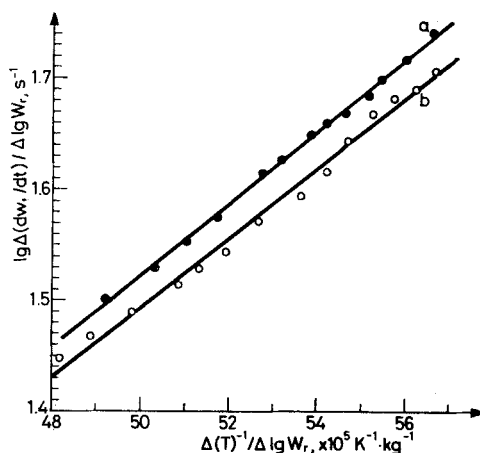

Fig. 2 Determination of activation energy E and reaction order n according to Freeman and Carroll [14]. a) $\varphi = 2.97$ deg/min and b) $\varphi = 8.48$ deg/min, providing two extremal values of activation energy

for $n \neq 1$, and

$$\log \left[\frac{-\log (1-\alpha)}{T^2} \right] = \log \frac{AR}{\varphi E} \left[1 - \frac{2RT}{E} \right] - \frac{E}{2.3RT} \tag{13}$$

for $n = 1$.

Equations (12) and (13) can be applied for determination of the activation energy E and coefficient A when $E \gg 2RT$. The method requires a correct value of n to obtain a straight-line relation with a slope of $-\dfrac{E}{2.3R}$. By choosing n in the range $+2$ to -2, an alteration of the regression coefficient (second digit after the point), activation energy E and frequency coefficient A was obtained (Table 1).

Table 1 Activation energy E, frequency factor A and regression coefficient computed according to Coats and Redfern [16] for different n values. Heating rate $\varphi = 2.97$ deg/min

n	E, kJ/mol	A, s^{-1}	ln A	r
2	137.4	6×10^{17}	40.9	-0.9763
1	88.5	9×10^9	22.9	-0.9841
0.78	83.1	7×10^8	20.4	-0.9878
0.5	82.8	2×10^9	21.5	-0.9948
0.1	66.8	7×10^6	15.8	-0.9941
0	66.5	1×10^7	16.4	-0.9964
-0.1	66.0	5×10^6	15.5	-0.9962
-1	41.1	4×10^3	8.4	-0.9889
-2	32.3	2×10^1	2.9	-0.9698

According to [9] and [17], simple decomposition processes can be described with another function $f(\alpha)$. With the Coats and Redfern approach to the function

$$f(\alpha) = \alpha^m \tag{14}$$

and

$$f(\alpha) = [-\ln (1-\alpha)]^{-1} \tag{15}$$

the following relations can be obtained

$$\ln \left[\frac{\alpha(1-m)}{T^2(1-m)} \right] = C - \frac{E}{R} \left(\frac{1}{T} \right) \tag{16}$$

and

$$\ln \left[\frac{(1-\alpha) \ln (1-\alpha) + \alpha}{T^2} \right] = C - \frac{E}{R} \left(\frac{1}{T} \right) \tag{17}$$

where

$$C = \ln \frac{AR}{\varphi E} \left[1 - \frac{2RT}{E} \right]$$

The values of the activation energy E and frequency factor A calculated according to relations (16) and (17) are included in Table 2. Herein, a change of $f(\alpha)$

Table 2 Activation energy E, frequency factor A and regression coefficient r computed following the Coats and Redfern method [16] according to relations (16), (17) and (20)

$f(\alpha)$	E, kJ/mol	A, s^{-1}	$\ln A$	r
$\alpha^{0.5}$	31.3	7×10^1	4.2	-0.9956
$[-\ln(1-\alpha)]^{-1}$	160.6	2×10^{20}	46.8	-0.9961
1	66.5	1×10^7	16.4	-0.9964

causes significant changes in E and A. Thus, for choice of the function $f(\alpha)$, an equation

$$\ln \frac{d\alpha}{dt} = \ln A + \ln [f(\alpha)] - \frac{E}{RT} \tag{18}$$

was applied. By representing $\ln \dfrac{d\alpha}{dt}$ vs. $\dfrac{1}{T}$ for six different heating rates for $\alpha = $ const., an activation energy E independent of the function $f(\alpha)$ was obtained. The energy $E = 61.2 \pm 5.6$ kJ/mol was found to be constant for three chosen values of α near 0.5. Obviously, such an activation energy determination provided an E value with a significant uncertainty. However, clearly shows that the function $f(\alpha) = 1$ (i.e. for $n = 0$, $m = 0$ and $P = 0$) describes the decompositon of the complex best.

In turn, assuming $f(\alpha) = 1$, the activation energy could be calculated from the Arrhenius relation (Fig. 3):

$$\ln \frac{d\alpha}{dt} = \ln A - \frac{E}{R} \left(\frac{1}{T} \right) \tag{19}$$

and according to Coats and Redfern Fig. 4:

$$\ln \frac{\alpha}{T^2} = \ln \frac{AR}{\varphi E} - \frac{E}{R} \left(\frac{1}{T} \right) \tag{20}$$

The value calculated from Eq. (19) is independent of the heating rate φ. The average value of the activation energy from six runs was found to be $E = 64.6 \pm 2.5$ kJ/mol.
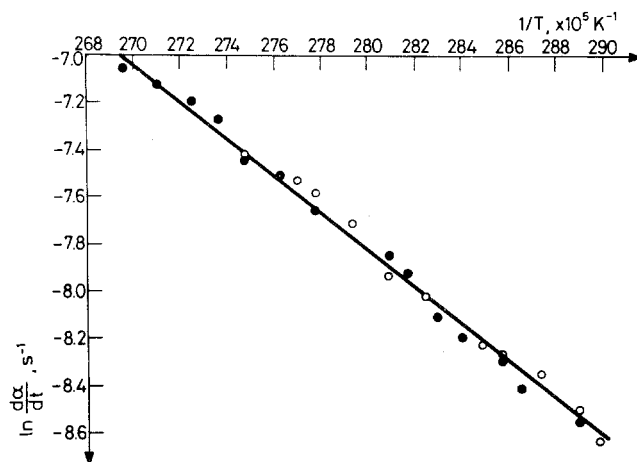
Fig. 3 Determination of activation energy E and frequency factor A from the Arrhenius equation. ● $\varphi = 4.71$ deg/min, ○ $\varphi = 2.97$ deg/min

In contrast, the activation energy obtained according to the Coats and Redfern method increased slightly with decrease of the heating rate. In order to obtain an E value more comparable to that under semi-isothermal conditions, a linear extrapolation of E values to $\varphi = 0$ was performed, and provided an E value of 65.7 ± 3.1 kJ/mol.

The kinetic parameters of the thermal decomposition of the β-cyclodextrin–water complex are included in Table 3. The methods used for

Table 3 Kinetic parameters of thermal decomposition of inclusion complex of water with β-cyclodextrin, computed according to the various methods employed

Method	Equat. no.	E, kJ/mol	n	A, s^{-1}	ln A	r
Kissinger	5.6	72.5	0.78*	6.8×10^7	18.0	−0.9999
Piloyan et al.	9	59.1		—	—	−0.9984
Freeman and Carroll	10	61.5*	−0.09*	—	—	−0.9972**
Independently of $f(\alpha)$						
for $\alpha =$ const.	18	61.2	—	—	—	−0.9874
Arrhenius equation						
for $f(\alpha) = 1$	19	64.6*	0	$1.3 \times 10^{6*}$	14.0*	−0.9925**
Coats and Redfern						
for $f(\alpha) = 1$	20	65.7***	0	$6.0 \times 10^{6***}$	15.6***	−0.8595

* an average value from 6 runs at different heating rates
** r value of the run closest to the average activation energy E
*** value of E extrapolated to $\varphi = 0$.

calculation yield only apparent kinetic parameters, which depend on the heating rates. Nevertheless, by using $f(\alpha) = (1-\alpha)^n$, the n values derived by means of different calculation techniques were quite consistent with each other, with the exception of the Kissinger method. All of them gave n values near to zero, which allow one to consider that $f(\alpha) = 1$ is a good approximation.

Like the reaction orders, the activation energies obtained via the different calculation techniques were closely similar. The lowest activation energy was
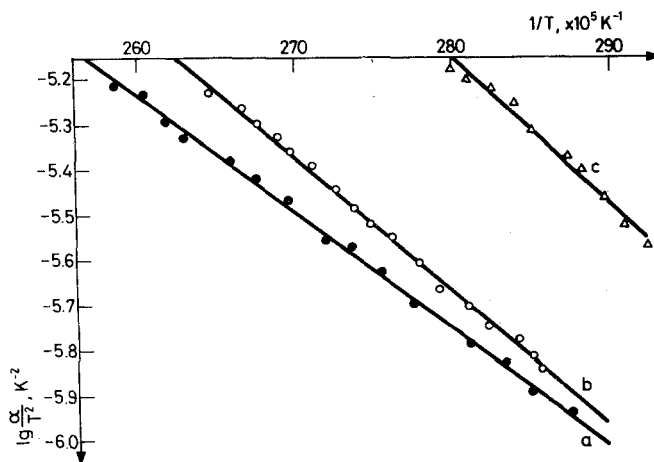

Fig. 4 Determination of activation energy E and frequency factor A according to Coats and Redfern for $f(\alpha) = 1$, a = 8.48 deg/min, b = 4.71 deg/min, c = 0.96 deg/min

obtained with the Piloyan method, although a slight decrease of the heating rate increased the activation energy significantly. Therefore, this method cannot be used for the reliable determination of the activation energy under semi-isothermal conditions. In turn, the highest activation energy obtained according to the Kissinger method is most probably due to small shift between the DTA and DTG curves. The best results for the activation energy were obtained with the Coats and Redfern approach. Only two parameters are required, the loss in weight W_t and the temperature T. This method gave only a slight change in activation energy with heating rate, which enables one to extrapolate the energy values to semi-isothermal conditions. This value was found to be 65.7 kJ/mol for $n = 0$, with a pre-exponential factor of 6×10^6 s $^{-1}$.

The loss in weight when water escapes from the cyclodextrin complex indicates that the composition of the complex is $(C_6H_{10}O_5)_7 \cdot 11.1H_2O$, which is consistent with the results of X-ray [18, 19] and neutron [20] diffraction studies. Although the

11 water molecules are shared between the cavity of cyclodextrin (6.13 molecules) and the external interstices (4.88 molecules), total water was liberated in one stage during thermal decomposition experiments.

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Zusammenfassung — Auf Grundlage von thermogravimetrischen Daten wurden die scheinbaren kinetischen Parameter des Thermozerfalles von β-Cyclodextrin-Wasser-Komplexen geschätzt. Die durch verschiedene Rechenmethoden erhaltenen Ergebnisse wurden in Tabelle 3 verglichen. Mit Ausnahme der Kissinger-Methode ergaben alle Verfahren eine Reaktionsordnung von annähernd Null und eine Aktivierungsenergie im Bereich 60–65 kJ/mol. Ausserdem wurde versucht, die Aktivierungsenergiewerte auf halbisotherme Bedingungen zu extrapolieren (65.7 kJ/mol). Der Masseverlust weist elf Wassermoleküle im Komplex nach, die in einem einzigen Schritt abgegeben werden, ungeachtet dessen, dass kristallographische Untersuchungen die Wassermoleküle zwei verschiedenen Typen zuordnen.

Резюме — На основе термогравиметрических данных были установлены кажущиеся кинетические параметры реакции термического разложения комплекса β-циклодекстрин-вода. Расчет таких параметров был проведен с использованием различных методов, а полученные при этом значения были сопоставлены. За исключением метода Киссинджера, остальные методы дают порядок реакции близкий к нулевому, а энергии активации — в интервале 60–65 кдж·моль$^{-1}$. Проведены некоторые попытки экстраполирования значений энергии активации к полуизотермическим условиям (65,7 кдж·мол$^{-1}$). Потери веса указывают на наличие в комплексе одинадцати молекул воды, выделяющиеся в одну стадию, хотя, как показали кристаллографические исследования, эти молекулы воды существуют в виде двух разных форм.