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KINETIC STUDY ON THE THERMAL DECOMPOSITION OF D-XYLOSE

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ABSTRACT

The kinetics of thermal decomposition of D-xylose have been elucidated by three methods. In the gas chromatographic method, the activation energy is 29.92 kcal mole^{-1}, the orders of reaction are 1.4 at 160°C, 1.6 at 170°C, 1.7 at 180°C and 1.8 at 190 and 200°C, and ln $A = 27.29$. In Ozawa's method, the activation energy is 29.19 kcal mole^{-1}, the order of reaction is 1.66 and ln $A = 26.46$. In Friedman's method, the activation energy is 29.22 kcal mole^{-1}, the order of reaction is 1.73 and ln $A = 28.97$.

INTRODUCTION

The kinetic analyses of many thermal decomposition reactions have been investigated. These analysis methods propose to estimate kinetic parameters from thermogravimetric data, and have been divided into several classes [1,2].

From these many methods, Ozawa's method [3], which is of the integral type, and Friedman's method [4], which is of the differential type, are employed here together with a gas chromatographic method which will be described later. The most important stage in the thermal decomposition of the sugar may be in the temperature range between the first and the second endotherms. The thermal behavior at this stage has already been reported [5–7]. To elucidate the kinetics of the thermal decomposition of the sugar, the application of three methods will be discussed in this paper.

EXPERIMENTAL

D-Xylose (G.R. grade), *meso*-erythrite (G.R. grade) and pyridine (G.R. grade) were purchased from Wako Junyaku Co. Ltd. Pyridine was dried and distilled at 115.5°C. Trimethylchlorosilane and hexamethyldisilazane were of gas chromatographic grade from Kanto Kagaku. Co. Ltd. In the gas chro-

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matographic method, samples of pyrolysis products of the sugar were prepared as described. Sugar samples weighing 35 mg were placed in the DTA furnace and heated at temperatures of 160, 170, 180, 190 and 200°C using a heating rate of 10°C min^{-1} and held at each temperature for 5–120 min. These samples were immediately taken out from the furnace and put into a dessicator cooled to −2°C, in order to stop thermal decomposition of the sugar as soon as possible. These samples were dissolved in 0.3 ml of pyridine. The solutions were trimethylsilylated with 0.2 ml of hexamethyldisilazane and 0.2 ml of trimethylchlorosilane. The solutions were vigorously stirred and allowed to stand for 30 min. An aliquot of 1 μl of a solution was injected into the gas chromatographic column. Gas chromatography was performed at a temperature programme of 150 to 230°C at 5°C min^{-1} on a Shimazu GC 4CPT equipped with TCD detectors (heated at 250°C) and stainless steel columns (3 mm × 3 m) packed with 3% SE-30 silicon gum, supported by chromosorb W on 80–100 mesh. Helium was used as the carrier gas at a flow rate of 30 ml min^{-1}. The peaks of the sugar appeared at 14.3 min (retention time) for the α-anomer and 16.5 min for β-anomer. In order to analyse quantitatively the amounts of the sugar in the pyrolysis products, *meso*-erythrite was used as an internal calibration standard. Samples of the sugar (3.3–23.4 mg) and *meso*-erythrite (1.1–4.0 mg) were exactly weighed, dissolved in pyridine and derivatized as already described.

From the results of gas chromatography, the ratios of total peak area of the sugar versus peak area of the internal standard were plotted against the ratios of the weight of the sugar versus the internal standard, as shown in

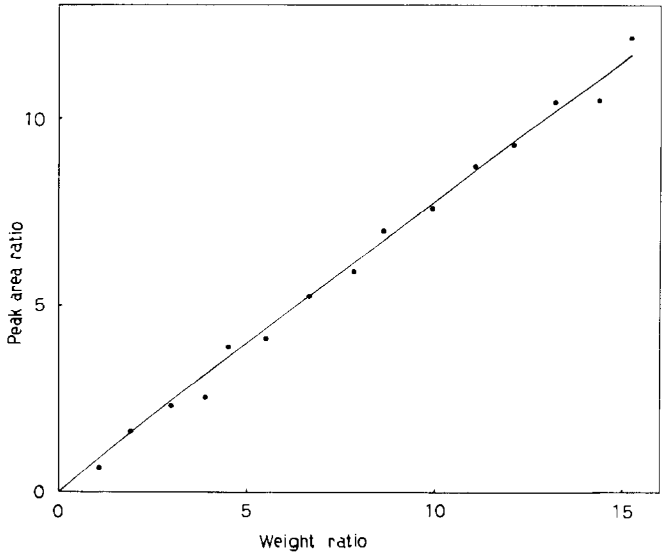

Fig. 1. Calibration curve of peak area ratio vs. weight ratio between D-xylose and the internal standard.

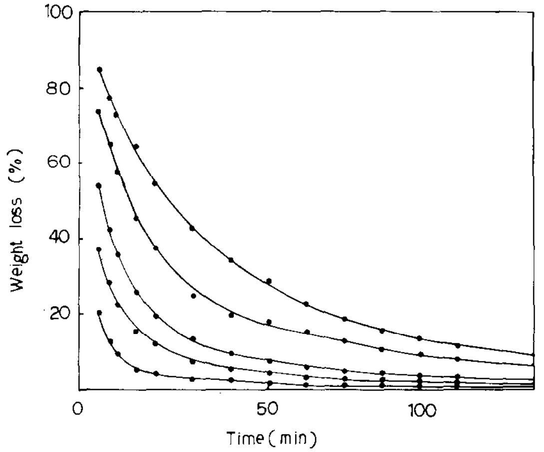

Fig. 2. Relation between the residual weight percentage of D-xylose and the pyrolysis time using the results from gas chromatography.

Fig. 1. Residual weight percentages of the sugar in pyrolysis products were determined as shown in Fig. 2. Differential thermal analysis and thermogravimetric measurements were carried out at a heating rate of 10°C min^{-1} in air on a Shimazu DTA 20B and TG 20. The results are shown in Fig. 3.

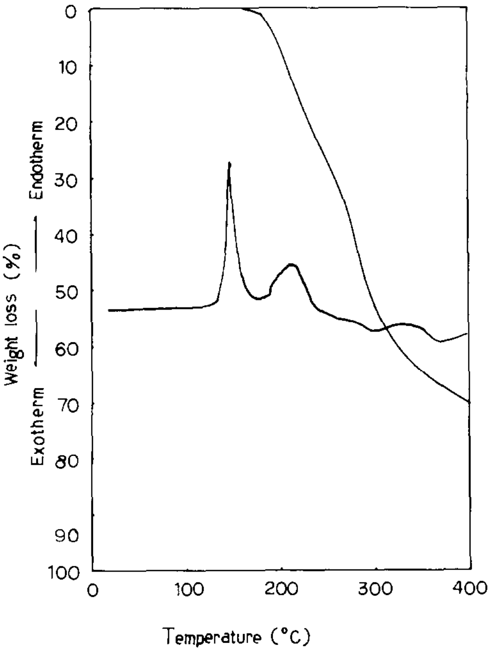

Fig. 3. DTA and TG curves of D-xylose at the heating rate of 10°C min^{-1} in air.

Thermogravimetric curves were recorded at heating rates of 0.5, 1, 2, and 5°C min^{-1} in air, as shown in Fig. 4. In addition to the preparation of samples by the gas chromatographic method as described, 30 mg of the sugar were heated at 190°–300°C. The products of each pyrolysis of the sugar were dissolved in 10 ml of water. The turbidity of the aqueous solutions was measured at 520 nm [7] and changed from 100% in the solution of pyrolysis products at 190°C down to 43% in the solution at 250°C and reaching up to 100% again in the solution at 280°C. Consequently, this indicates that the residual weight at 280°C, shown in the thermogravimetric curve in Fig. 3, corresponds to the value of w_f which is the final weight of char in Friedman's equation [4], i.e. $w_f/w_0 = 0.614$.

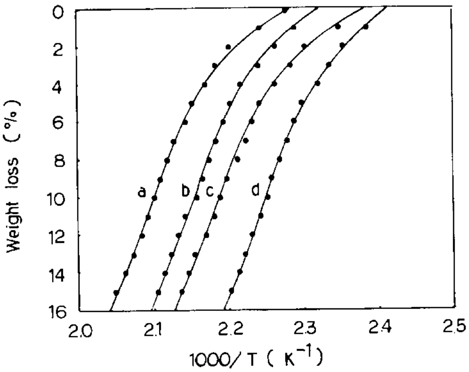

Fig. 4. TG curves of D-xylose against the reciprocal absolute temperature at heating rates (°C min^{-1}) of: a, 0.5; b, 1; c, 2 and d, 5.

RESULTS AND DISCUSSION

In the gas chromatographic method, kinetic parameters were evaluated from the relation between the residual weight of the sugar and time, at each pyrolysis temperature.

In the thermal decomposition reaction $A(s) \rightarrow B(s) + C(g)$ the kinetic equation is expressed as

$$\frac{-dw}{dt} = k(1-w)^n \tag{1}$$

where w is the weight of A decomposed at time t, and n is the order of reaction.

Integrating eqn. (1) and rearranging, we get

$$k = \frac{\left[1 - \frac{1}{(1-w)^{n-1}}\right]}{t(n-1)} \tag{2}$$

TABLE 1

Orders of reaction, rate constants and ln *A* values obtained from the gas chromatographic method

Heating temp. (°C)	Order of reaction	Rate constant *k*	ln *A*
160	1.4	5.629×10^{-4}	27.35
170	1.6	1.058×10^{-3}	27.20
180	1.7	2.499×10^{-3}	27.30
190	1.8	4.840×10^{-3}	27.25
200	1.8	1.044×10^{-2}	27.33

The order of reaction, n, should be selected such that calculation of the rate constant, k, by use of eqn. (2), gives a constant value.

From the gas chromatography data, the results of thermal decomposition reactions of the sugar are shown in Table 1. These results show that in pyrolysis at every given temperature (160–200°C), the order of reaction becomes gradually larger; $n = 1.4$ at 160°C, 1.6 at 170°C, 1.7 at 180, 190 and 200°C.

The rate constant is expressed as $k = Ae^{-E/RT}$ according to the Arrhenius equation, where A is the pre-exponential factor, E is the activation energy, T is the absolute temperature, and R is the gas constant.

Taking logarithms of the Arrhenius equation gives

$$\ln k = \ln A - \frac{E}{RT} \tag{3}$$

The logarithms of the rate constants are plotted against the reciprocal absolute temperatures in Fig. 5. This straight line plot was determined by the

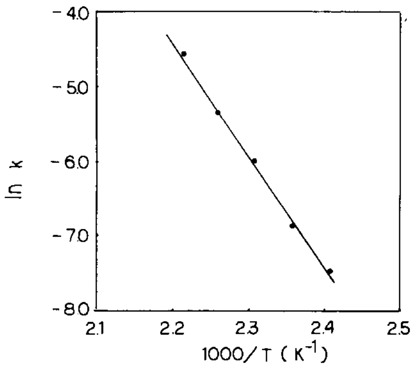

Fig. 5. Arrhenius plots of the logarithms of the rate constant against the reciprocal absolute temperature using the results of gas chromatography.

least squares method. The activation energy, as evaluated from the slope, was $E = 29.92$ kcal mole^{-1}. The value of ln A was also determined by use of eqn. (3) and found to be 27.29 and $A = 7.07 \times 10^{11}$ sec^{-1}.

Ozawa has derived an equation under the condition of Doyle's approximation [8]

$$\ln \alpha = \ln\left(\frac{AE}{R}\right) - \ln\left(4.339 \times 10^{-3}\, I_n\right) - \frac{1.052E}{RT} \tag{4}$$

where α is the heating rate, $I_n = -\int \mathrm{d}w/w^n$, and n is the order of reaction. Thermogravimetric curves are plotted against reciprocal absolute temperatures for each heating rate in Fig. 4. The logarithms of the heating rates are plotted against the reciprocal absolute temperatures in Fig. 6. The straight line plots in Fig. 6 are determined by the least squares method. Activation energies are evaluated from the slopes of the lines which are equal to $-1.052E/R$. The mean of the activation energies is 29.19 kcal mole^{-1}. The values of E/RT are in the range 29.83–33.28. Since it is difficult to determine accurately the order of reaction in the narrow temperature range

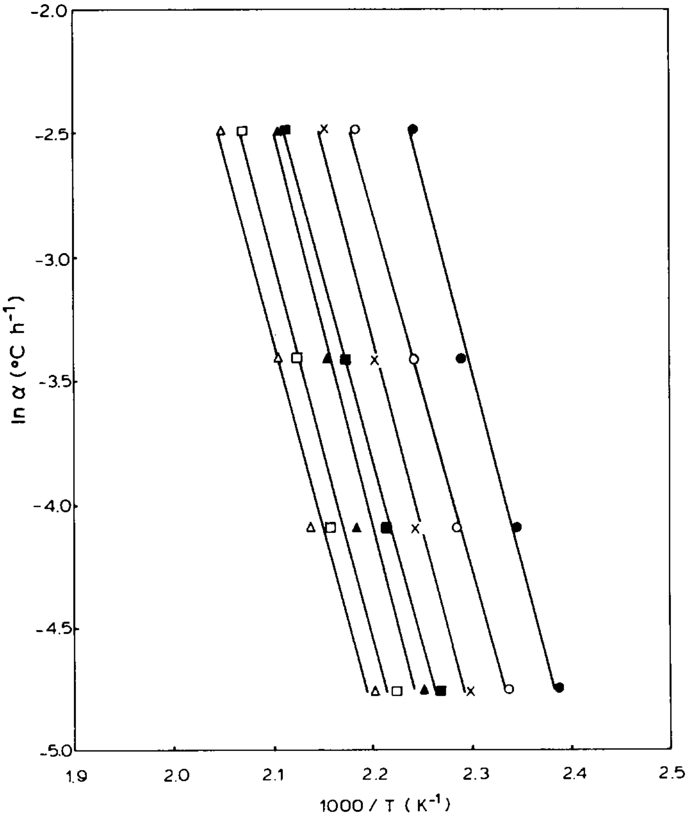

Fig. 6. Plots of the logarithms of heating rate vs. reciprocal absolute temperature obtained from TG data at weight losses (%) of: △, 15; □, 13; ▲, 10; ■, 8; ×, 5; ○, 3; ●, 1.

between the first and the second endotherm in this method, the order of reaction employed is 1.66, which is the mean of the n values obtained from the gas chromatographic method. The value of ln A is evaluated as 26.46 and $A = 3.11 \times 10^{11}$ sec^{-1}.

Friedman has proposed the relationship

$$\ln\left[-\frac{1}{w_0}\frac{\mathrm{d}w}{\mathrm{d}t}\right] = \ln\left[\frac{A(W - w_f)}{w_0}\right] - \frac{E}{RT} \tag{5}$$

where w_0 is the weight of the sugar at time $t = t_0$, w is the weight of the sugar at time t, and w_f is the weight of the sugar pyrolysed at 280°C, as discussed above. The logarithms of $[-(1/w_0)\ \mathrm{d}w/\mathrm{d}t]$ are plotted against reciprocal absolute temperatures in Fig. 7. The straight line plots obtained in Fig. 7 are determined by the least squares method. Activation energies are evaluated from the slopes of the straight lines and the mean of these is 29.22 kcal mole^{-1}. In order to elucidate the order of reaction and the pre-exponential factor, the form

$$\ln\left[A\mathrm{f}\left(\frac{w}{w_0}\right)\right] = \ln A + n\ln\left[\frac{w - w_f}{w_0}\right] \tag{6}$$

has been proposed. Plots of the logarithms of $[A\mathrm{f}(w/w_0)]$ against the logarithms of $[(w - w_f)/w_0]$ give a straight line, as shown in Fig. 8, except when values of $\ln[(w - w_f)/w_0]$ lie in the range 1.00–0.96. The slope of the line in Fig. 8 corresponds to the order of reaction, i.e. $n = 1.73$. The

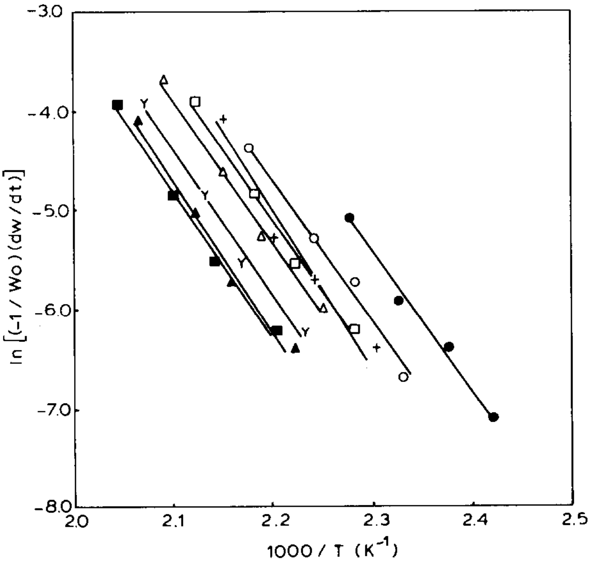

Fig. 7. Arrhenius-type plots of $\ln[-(1/w_0)\ \mathrm{d}w/\mathrm{d}t]$ vs. reciprocal absolute temperature at w/w_0 values of: ●, 0.99; ○, 0.97; ×, 0.95; □, 0.93; △, 0.90; Y, 0.88; ▲, 0.87; ■, 0.85.

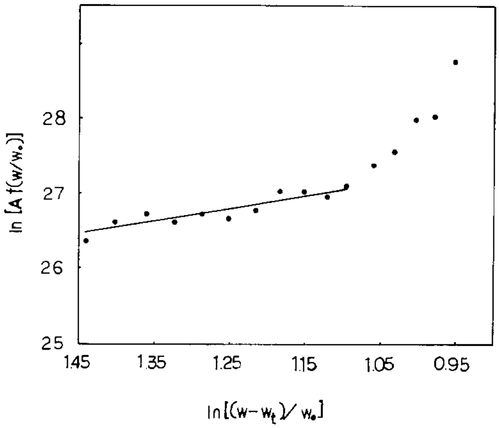

Fig. 8. A plot of $\ln[Af(w/w_0)]$ vs. $\ln[(w-w_f)/w_0]$.

logarithms of A are calculated by subtraction of 1.73 times the logarithms of $[(w-w_f)/w_0]$ from the logarithms of $[Af(w/w_0)]$. Consequently, the mean of the logarithms of A is 28.97 and $A = 3.81 \times 10^{12}$ sec^{-1}.

The results of the three methods suggest that the activation energy values are in good agreement with each other. Orders of reaction, as shown by the gas chromatographic method, exist between 1.4 and 1.8 at pyrolysis temperatures of 160°–200°C; the value from Friedman's method is 1.73. The logarithms of A are: 26.46 by Ozawa's method, which is the minimum value, 28.97 by Friedman's method, which is the maximum, and 27.29 by the gas chromatographic method, which shows the mean value.

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