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KINETIC STUDY ON THE THERMAL DECOMPOSITION OF CYTIDINE AND URIDINE

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ABSTRACT

Thermal decompositions of cytidine and uridine were investigated from room temperature to 450 ° C. Kinetics of the decomposition in two samples have been elucidated by Friedman's and Tanaka's methods.

In Friedman's method, the activation energy is 40.35 kcal mol^{-1} for cytidine and 37.21 kcal mol^{-1} for uridine, the order of reaction is 1.68 for cytidine and 1.59 for uridine, and ln Z is 38.63 for cytidine and 33.50 for uridine. In Tanaka's method, the activation energy is 40.69 kcal mol^{-1} for cytidine and 37.18 kcal mol^{-1} for uridine, and ln Z is 36.63 for cytidine and 32.19 for uridine.

INTRODUCTION

Thermal behaviour of carbohydrates has been discussed from DTA data in Morita's studies [1]. Thermal decomposition products of carbohydrates have been investigated by Shafizadeh and Lai [2] and Houminer and Patai [3]. In thermal decomposition of carbohydrates, weight loss begins near the first endotherm and decomposition is facilitated and terminates at the second endotherm [4,5]. To elucidate the kinetics of thermal decomposition of carbohydrates, it is very important that TG curves at every heating rate change between the first and the second endotherm [4–6].

There have been many kinetic methods in thermal decomposition and degradation. These have been discussed in detail and described in general considerations by Flynn and Wall [7] and Šesták et al. [8]. The kinetics obtained from TG curves are classified into several types: typically integral, differential and difference–differential. Very careful treatments are demanded for the elucidation of kinetics in thermal decompositions. It has been pointed out that more than two methods are utilized to estimate kinetic

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parameters and, if values of parameters coincide with each other, these values will not be false [7], however, the activation energy estimated for a system where the reaction order changes will be erroneous [9].

In continuation of our studies [5,6] on the kinetics of the thermal decomposition of carbohydrates, we have investigated the kinetics of thermal decomposition of cytidine and uridine by application of two methods and the results will be discussed and described in this paper.

EXPERIMENTAL

Cytidine (GR grade) and uridine (GR grade) were purchased from Wako Junyaku Co. Ltd. Ten milligrammes of cytidine and uridine were used for DTA and TG at a heating rate of 10 °C min^{-1} on a SHIMAZU DTA 20B and a TG 20. In order to elucidate kinetic parameters in the thermal decomposition of cytidine and uridine, TG curves were recorded at heating rates of 1, 2 and 5 °C min^{-1}, using 5 mg for each of the two samples. The samples were conserved in a desiccator at room temperature under a reduced pressure of 10^{-3} mmHg. All measurements in DTA and TG were carried out in air.

RESULTS AND DISCUSSION

The results of DTA and TG of cytidine are shown in Fig. 1. The DTA curve shows the first endotherm at 216 °C, the melting point, the second at 242 °C and the exotherm at 273 °C. The TG curve shows that weight loss begins near 220 °C, rapidly drops from 3 to 38% between 230 and 290 °C,

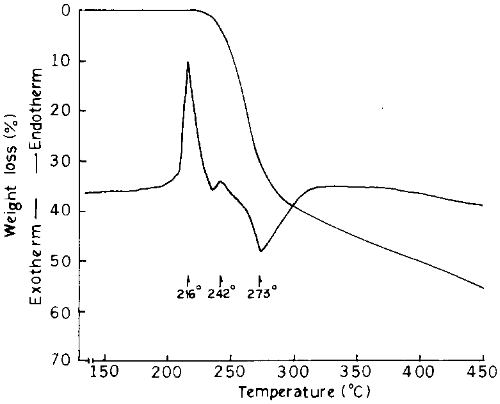

Fig. 1. DTA and TG curves of cytidine (10 mg) at the heating rate $f = 10$ °C min^{-1} in air.

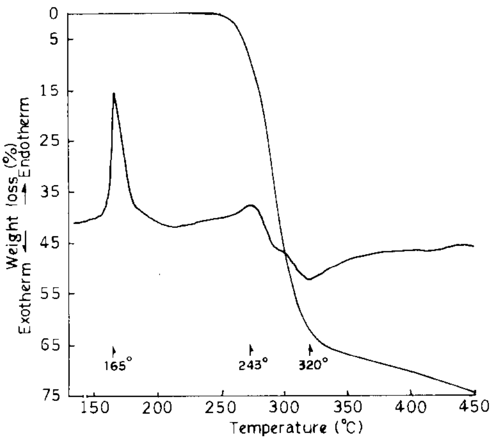

Fig. 2. DTA and TG curves of uridine (10 mg) at the heating rate of 10°C min^{-1} in air.

and gradually decreases at a temperature higher than 300°C. The results of DTA and TG of uridine are shown in Fig. 2. The DTA curve shows the first endotherm at 165°C, the second at 273°C and the exotherm at 320°C. The TG curve shows that weight loss does not change up to the end of the first endotherm, begins at 225°C, rapidly drops from 2 to 65% between 260 and 330°C and gradually decreases at a temperature higher than 330°C. These results suggest that the decomposition of the samples begins near the first endotherm and terminates at the second endotherm, and more complex decomposition of pyrolysis products, observed by heating to the second endotherm, is facilitated at a temperature higher than this latter endotherm.

TG curves of cytidine and uridine are plotted against reciprocal absolute temperature, at the three heating rates, to estimate the kinetics in the thermal decomposition by use of Friedman's [10] and Tanaka's [6] method (Figs. 3 and 4).

Friedman [10] has shown the following equations:

$$\ln[(-1/w_0)(\mathrm{d}w/\mathrm{d}t)] = \ln[Zf(w/w_0)] - \Delta E/\mathrm{R}T \qquad (1)$$

$$\ln[Zf(w/w_0)] = \ln Z + n \ln[(w - w_e)/w_0] \qquad (2)$$

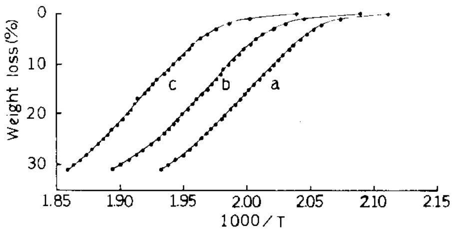

Fig. 3. TG curves of cytidine. Plots of weight loss against $1000/T$ at the heating rates (°C min^{-1}) of: a, 1; b, 2 and c, 5.

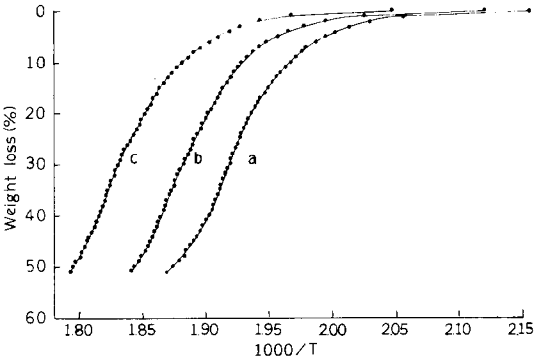

Fig. 4. TG curves of uridine. Plots of weight loss against $1000/T$ at the heating rates (°C $\min^{-1}$) of: a, 1; b, 2 and c, 5.

where w_0 = weight of sample at time $t = t_0$, w = weight at t, Z = pre-exponential factor, T = absolute temperature, R = gas constant, ΔE = activation energy, w_e = weight of char, n = order of reaction.

The logarithms of $[(-1/w_0)(\mathrm{d}w/\mathrm{d}t)]$ are plotted against reciprocal absolute temperatures in Figs. 5 and 6. Straight lines are determined by the least squares method. Activation energies are estimated by the slopes of the lines. The mean is 40.35 kcal mol^{-1} (1–29% in weight loss) in cytidine and 37.21 kcal mol^{-1} (1–47% in weight loss) in uridine (see Figs. 7 and 8). The activation energy suddenly becomes large at a weight loss larger than 30% in cytidine and 50% in uridine. These facts suggest that the thermal decomposition of samples terminates at the above-mentioned weight losses and, successively, more complicated decomposition reactions occur at a weight loss larger than 30% in cytidine and 50% in uridine. The logarithms of $[Zf(w/w_0)]$, as functions of w/w_0, are the intercepts of the straight lines obtained. These values are plotted against the weight loss in Figs. 7 and 8. Inclinations in the values of ΔE and the logarithms of $[Zf(w/w_0)]$ are identical in cytidine and uridine, as Friedman pointed out.

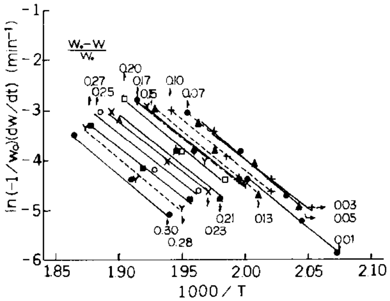

Fig. 5. Arrhenius-type plots of $\ln(-1/w_0)(\mathrm{d}w/\mathrm{d}t)$ against $1000/T$ in cytidine.

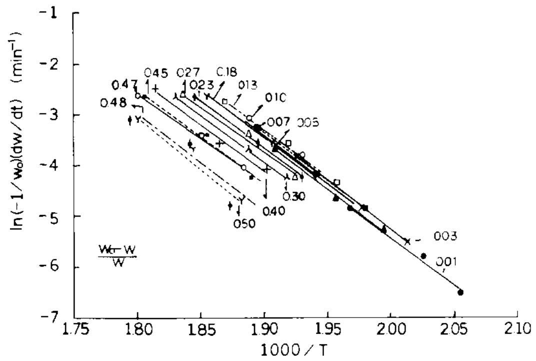

Fig. 6. Arrhenius-type plots of $\ln(-1/w_0)(\mathrm{d}w/\mathrm{d}t)$ against $1000/T$ in uridine.

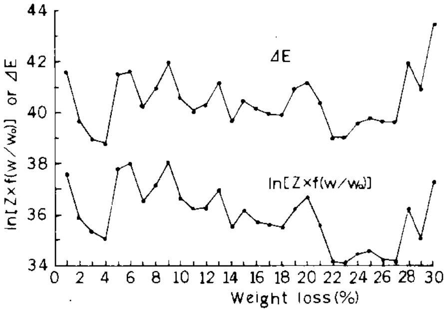

Fig. 7. Plots of E against weight loss in cytidine.

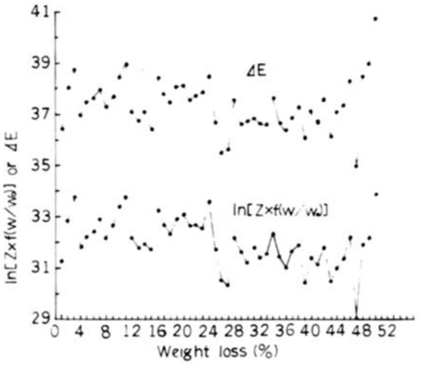

Fig. 8. Plots of E against weight loss in uridine.

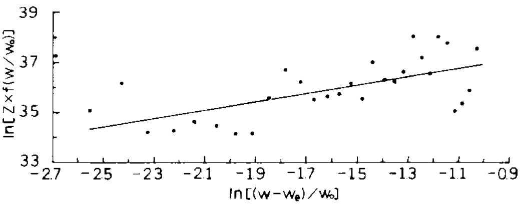

Fig. 9. Plots of $\ln[Zf(w/w_0)]$ against $\ln[(w-w_c)/w_0]$ in cytidine.

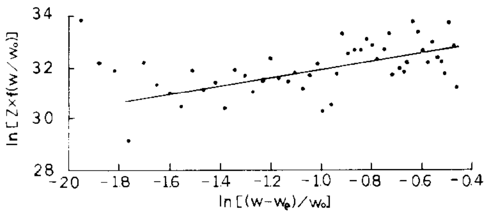

Fig. 10. Plots of $\ln[Zf(w/w_0)]$ against $\ln[(w-w_e)/w_0]$ in uridine.

In order to elucidate order of reaction and pre-exponential factor, the second term of eqn. (1) is given as eqn. (2) and the logarithms of $[Zf(w/w_0)]$ are plotted against the logarithms of $[(w-w_e)/w_0]$ (Figs. 9 and 10). The straight lines in cytidine and uridine are determined by the least squares method. The slopes of the lines correspond to the order of reaction, i.e. $n = 1.68$ in cytidine and 1.59 in uridine, and the logarithms of Z, which are the intercepts in the lines, are 38.63 in cytidine and 33.50 in uridine, within the above ranges in the weight loss. Here the values of w_e are taken to be the residual weights of 3.16 mg at 273°C in cytidine and 1.79 mg at 320°C in uridine.

Tanaka [6] has proposed the relationship

$$\ln \beta = \ln \frac{Z}{\alpha + n\alpha^2/2 + n(n+1)\alpha^3/6} \frac{\Delta E}{\mathrm{R}} \frac{p(u)}{\exp(-u)} - \frac{\Delta E}{\mathrm{R}T} \tag{3}$$

where β = heating rate, α = fraction of decomposed sample, $u = \Delta E/\mathrm{R}T$ and

$$p(u) = \frac{\exp(-u)}{u} \frac{u^2 + 11u + 16}{u^3 + 13u^2 + 36u + 19} \tag{4}$$

The logarithms of the heating rates are plotted against the reciprocal absolute temperatures in Figs. 11 and 12. Straight lines are obtained by the least squares method. Activation energies are evaluated from the slopes of the lines, which are equal to $-\Delta E/\mathrm{R}$. The mean is 40.69 kcal mol^{-1} (3–28% weight loss) in cytidine and 37.18 kcal mol^{-1} (1–47% weight loss) in uridine (Figs. 13 and 14).

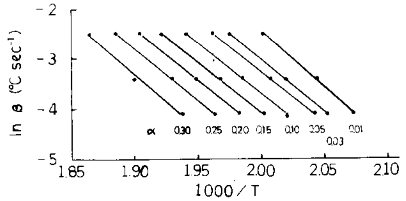

Fig. 11. Plots of ln β against $1000/T$ in cytidine.

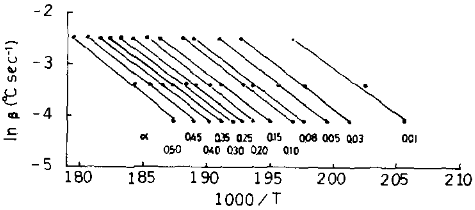

Fig. 12. Plots of ln β against 1000/T in uridine.

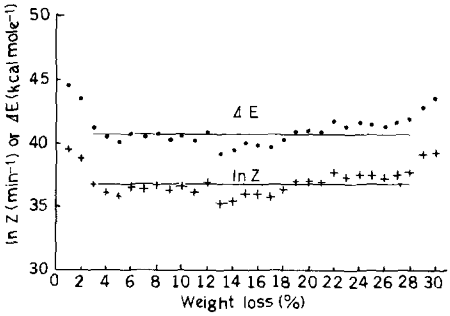

Fig. 13. Plots of ΔE and ln Z against weight loss in cytidine.

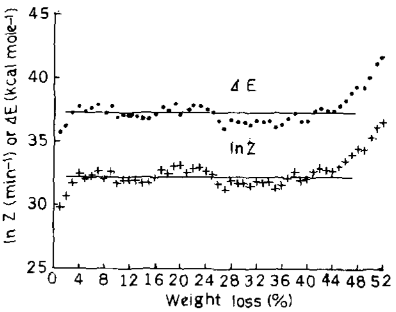

Fig. 14. Plots of ΔE and ln Z against weight loss in uridine.

TABLE 1

The relationship between the order of reaction and the decomposition temperature

Order of reaction	Temperature range (°C)	
	Cytidine	Uridine
1	217.0–222.0	165.0–186.6
1.25	222.0–227.0	186.6–208.2
1.5	227.0–232.0	208.2–229.8
1.75	232.0–237.0	229.8–251.4
2	237.0–242.0	251.4–273.0

TABLE 2

The kinetic parameters (ΔE, kcal mol^{-1}; ln Z, min^{-1}) for the two methods used

Sample	Kinetic parameter	Friedman's method	Tanaka's method
Cytidine	ΔE	40.35	40.69
	ln Z	38.63	36.63
	n	1.68	
Uridine	ΔE	37.21	37.18
	ln Z	33.50	32.24
	n	1.59	

Orders of reaction are determined from the first and the second endotherm, as discussed in Ref. 6 and shown in Table 1.

When using eqn. (4) it was ensured that only the region where $u \geqslant 0.48$ was considered. In our case, the region of u is 39.68–42.59 for cytidine and 34.71–38.17 for uridine, in order for the values of u to be satisfactory. The logarithms of Z are estimated from eqn. (4) and the mean is 36.63 (for the above weight loss) in cytidine and 32.19 (for the above weight loss) in uridine (Figs. 13 and 14).

The results of the kinetic parameters estimated are shown in Table 2 and are consistent with each other in the two methods.

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