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Note

KINETIC STUDY OF THE THERMAL DECOMPOSITION OF ADENOSINE

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The thermal analysis of adenosine was made by use of differential thermal analysis (DTA) and thermogravimetric (TG) data in the region between room temperature and 500 °C. The kinetic parameters of the thermal decomposition of adenosine were evaluated by using Friedman's and the author's own methods. With Friedman's method, the activation energy was 210.31 kJ mol^{-1}, the order of reaction 1.79, and $\ln Z = 47.88$. With the author's own method, the activation energy was 209.88 kJ mol^{-1}, the mean value of the order of reaction was 1.63, and $\ln Z = 44.38$.

EXPERIMENTAL

Adenosine was of G.R. grade (Wako Junyaku Co. Ltd.) and used without further purification. A Shimazu 20B and TG were used for direct thermal analysis (DTA) and thermogravimetric (TG) measurements.

In order to evaluate the kinetic parameters of the thermal decomposition of adenosine, TG curves were recorded at heating rates of 1, 2 and 5 °C min^{-1} using 5 mg of sample. All DTA and TG measurements were carried out in air at ambient pressure.

RESULTS AND DISCUSSION

The results of the DTA and TG of the sample at a heating rate of 10 °C min^{-1} are shown in Fig. 1. The DTA curve shows a first endotherm at 237 °C (the melting point), a second at 262 °C and an exotherm at 288 °C. The TG curve shows that weight loss begins near 240 °C, with the weight rapidly decreasing from 3 to 30% between 257 and 291 °C, more slowly between 308 and 452 °C, and decreases again at temperatures above 450 °C.

These results suggest that the thermal decomposition of the sample begins near the first endotherm, terminates near the second endotherm, and occurs

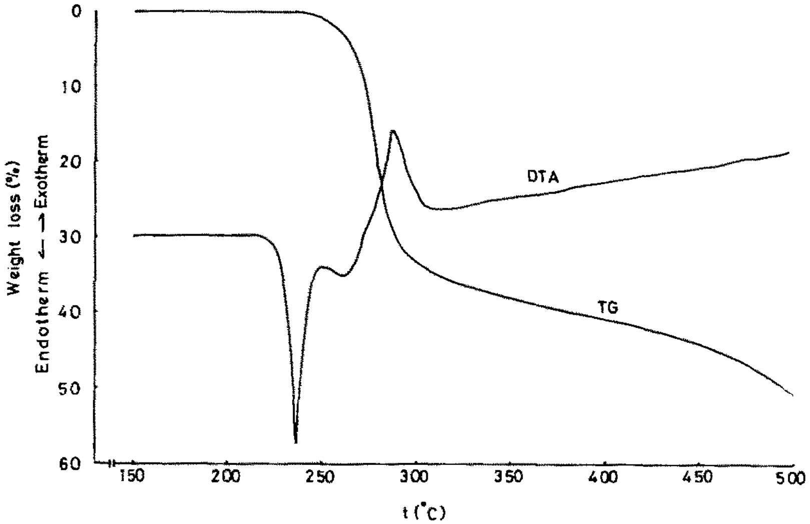

Fig. 1. DTA and TG curves at a heating rate of 10 °C min^{-1}.

with a weight loss of less than 30% which is in agreement with the pattern shown for carbohydrates in general [1–3].

The TG curves are plotted against the reciprocal absolute temperatures for the three heating rates in Fig. 2.

Friedman [4] has shown the following equation:

$$\ln\left(\frac{-1}{w_0}\right)\frac{\mathrm{d}w}{\mathrm{d}t} = \ln\left[Zf\left(\frac{w}{w_0}\right)\right] - \frac{E}{RT}$$

$$= \ln Z + n \ln\left(\frac{w - w_c}{w_0}\right) - \frac{E}{RT} \qquad (1)$$

where w_0 is the weight of the sample at time $t = t_0$, w is the weight at t, Z is the pre-exponential factor, T is the absolute temperature, R is the gas

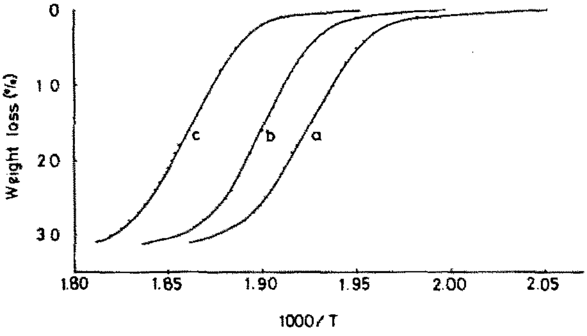

Fig. 2. TG curves of weight loss against $1000/T$ at the following heating rates; curve a, 1 °C min^{-1}; curve b, 2 °C min^{-1}; curve c, 5 °C min^{-1}.

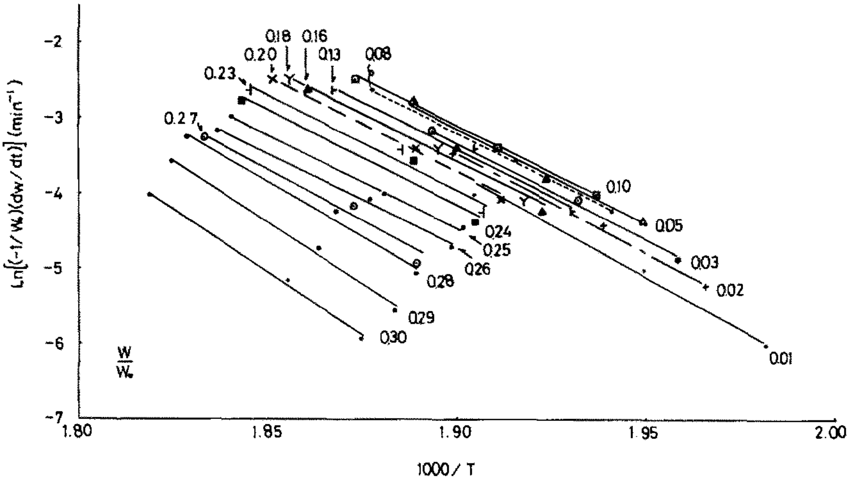

Fig. 3. Arrhenius-type plots of $\ln(-1/w_0)(\mathrm{d}w/\mathrm{d}t)$ against $1000/T$.

constant, E is the activation energy, w_c is the weight of char, and n is the order of reaction.

The absolute temperature and $(-1/w_0)(\mathrm{d}w/\mathrm{d}t)$ were determined at a constant w for the three heating rates. The logarithms of $(-1/w_0)(\mathrm{d}w/\mathrm{d}t)$ are plotted against the reciprocal absolute temperatures in Fig. 3. The straight lines were determined using the least-squares method. The slopes of lines are equal to $-E/R$.

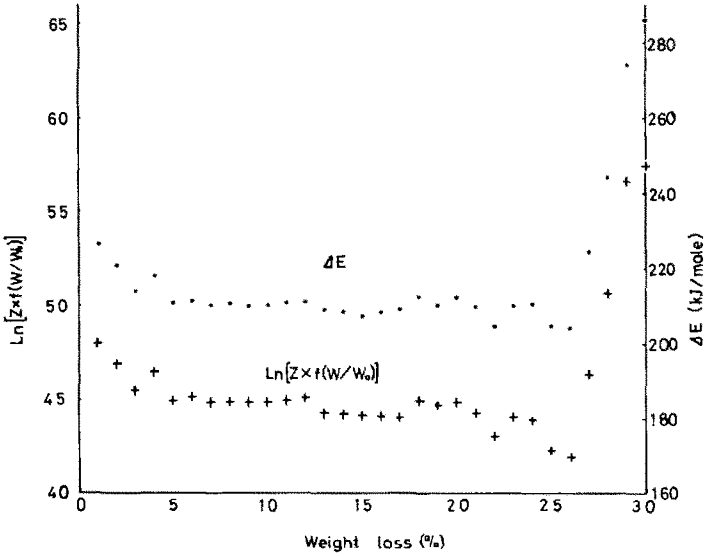

Fig. 4. Plots of E and $\ln[Zf(w/w_0)]$ against weight loss.

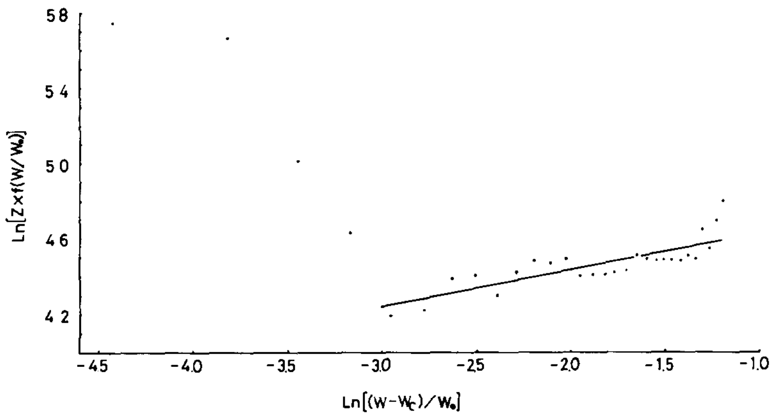

Fig. 5. Plots of $\ln[Zf(w/w_0)]$ against $\ln[(w-w_c)/w_0]$.

The activation energies were estimated from the plot shown in Fig. 4: mean value 210.31 kJ mol^{-1} (2–26% weight loss). At a weight loss of $> 27\%$, the activation energy increases (Fig. 4). This fact suggests that complicated decomposition reactions occur. The intercepts of the lines are given by $\ln[Zf(w/w_0)]$; the 25 values of $\ln[Zf(w/w_0)]$ were averaged to give 44.54. The trends in the values of $\ln[Zf(w/w_0)]$ and the activation energies for weight loss are identical in Fig. 4.

A plot of $\ln[Zf(w/w_0)]$ against $\ln[w-w_c)/w_0]$ is shown in Fig. 5. The value of w_c was taken to be the residual weight of 3.44 mg at 288 °C. The straight lines (2–26% weight loss) were determined using the least-squares method. The slope of the lines corresponds to the order of reaction: $n = 1.79$, intercept 47.88.

The author's equation [5] used in this work is

$$\ln\beta = \frac{\ln\left(\frac{ZE}{R}\right)}{\int d\alpha/(1-\alpha)^n} \frac{p(u)}{\exp(-u)} - \frac{E}{RT} \tag{2}$$

where β is the heating rate, and α the fraction of decomposed sample $(u = E/RT)$. The function of u is

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

and

$$\int \frac{d\alpha}{(1-\alpha)^n} = \alpha + \frac{n\alpha^2}{2} + \frac{n(n+1)\alpha^3}{6} \tag{4}$$

The logarithms of the three heating rates are plotted against the reciprocal absolute temperatures in Fig. 6. The straight lines were determined using the

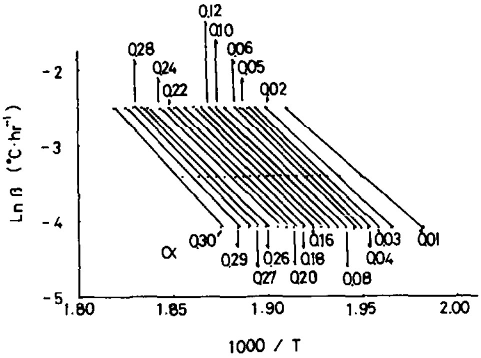

Fig. 6. Plots of ln β against $1000/T$.

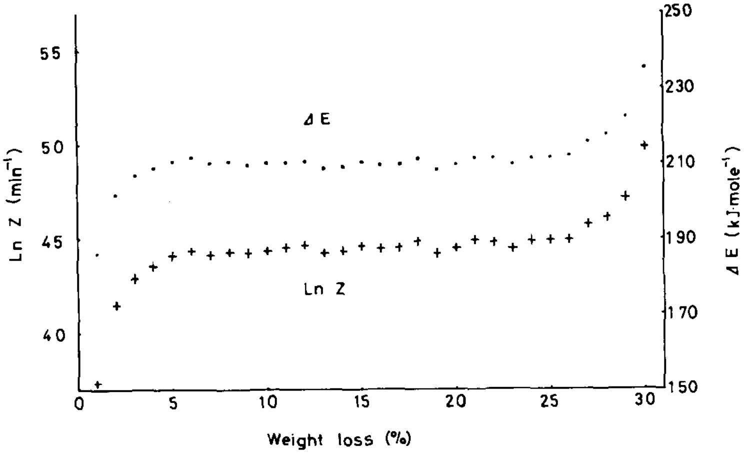

Fig. 7. Plots of E and ln Z against weight loss.

least-squares method and the slopes of the lines are equal to $-E/R$. The activation energies were evaluated and a mean value (209.88 kJ mol^{-1}; 2–26% weight loss) taken for use in Fig. 7.

The orders of reaction were determined as discussed in ref. 5 and shown in Table 1. The mean value obtained was 1.63 in the case of a heating rate of

TABLE 1

The relationship between the order of reaction n and the decomposition temperature

Order of reaction n	Temperature range (°C)
1	237–242
1.25	242–247
1.5	247–252
1.75	252–257
2	257–262

2° C $\min^{-1}$. The range of u was 47.73–49.48 and of α was 0–0.3; therefore the results are satisfactory because the conditions for application of eqns. (3) and (4) are $u \geqslant 0.48$ and $\alpha \leq 0.3$ in the temperature range studied. The logarithms of Z were evaluated using eqn. (2) and the results are shown in Fig. 7: mean value 44.30 (2–26% weight loss).

The results of the kinetic parameters evaluated with each method coincide.

REFERENCES

1 F. Örsi, J. Therm. Anal., 5 (1973) 329.
2 Y. Tanaka and T. Nakamura, Thermochim. Acta, 44 (1981) 303; 62 (1983) 307.
3 Y. Tanaka, N. Takeda and D. Fujita, Thermochim. Acta, 115 (1987) 281.
4 H.L. Friedman, J. Polym. Sci., Part C, 6 (1964) 183.
5 Y. Tanaka, Thermochim. Acta, 91 (1985) 299.