

THE THERMAL DECOMPOSITION OF ARBUTIN

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ABSTRACT

The thermal decomposition of arbutin starts at the melting at 200°C and terminates at 288°C. Non-volatile decomposition products are mainly hydroquinone(Hq), 1,6-anhydro-β-D-glucopyranose(16AGP), 1,6-anhydro-β-D-glucofuranose(16AGF) and α- and β-D-glucose.

In order to elucidate the kinetics, the methods of Friedman and Ozawa are applied for the thermal decomposition of arbutin. In Friedman's method, the activation energy is 26.27 kcal mol⁻¹, the order of reaction is 0.985 and $A = 6.94 \times 10^8 \text{ sec}^{-1}$. In Ozawa's method, the activation energy has an initial value of 27.87 kcal mole⁻¹, a minimum value of 26.50 kcal mole⁻¹ and a final average value of 27.61 kcal mole⁻¹, the order of reaction is 1, and $A = 1.55 \times 10^8 \text{ sec}^{-1}$.

INTRODUCTION

The thermal degradation of carbohydrates is complicated by the occurrence of intermolecular rearrangements and interactions in addition to dehydration and decomposition. A variety of approaches [1–9] have been tried on the pyrolysis of carbohydrates, characterizing a lot of pyrolysis products and proposing some courses of the reaction.

In continuation of our studies on the pyrolysis of pentose [7], we have investigated the thermal decomposition and kinetics of arbutin using DTA, TG, paper- and gas chromatography, and IR spectroscopy, the results of which are described here.

EXPERIMENTAL

Arbutin was of G.R. grade from Wako Junyaku Co. Ltd. 1,6-Anhydro-β-D-glucopyranose (16AGP) and 1,6-anhydro-β-D-glucofuranose (16AGF) were prepared by the pyrolysis of starch [8,9]. 16AGP (m.p. 182°C) was recrystallized from methanol [4]. 16AGF (m.p. 110°C) was separated from the pyrolysis products of starch using paper chromatography [10]. Chromatographic grade trimethylchlorosilane and hexamethyldisilazane were obtained from Kanto Kagaku Co. Ltd. The samples of the pyrolysis products of arbutin were prepared as follows: 50 mg of arbutin were heated to 220–325°C in

the DTA furnace at a heating rate of $10^{\circ}\text{C min}^{-1}$ and immediately taken out and placed in the desiccator cooled at -2°C . Paper chromatography of the pyrolysis products of starch was carried out on Toyoroshi No. 51 paper using a developing solvent mixture consisting of *n*-butanol–acetic acid–water (4 : 1 : 5) [11], and silver nitrate [13] spray was used to detect and obtain 16AGF ($R_f = 0.37\text{--}0.39$) [10]. Thus 16AGF was repeatedly prepared to obtain about 30 mg. In order to identify various products in the pyrolysed arbutin, solutions for paper chromatography were prepared by dissolving 30 mg of the pyrolysis products heated at $220\text{--}325^{\circ}\text{C}$ in 0.2 ml of water. The solutions were spotted on No. 51 papers. A developing mixed solvent consisted of *n*-butanol–pyridine–water (6 : 4 : 3) [12]. Silver nitrate [13] and potassium permanganate [14] were used. Ten mg of arbutin were used for DTA and TG at a heating rate of $10^{\circ}\text{C min}^{-1}$ on a Shimadzu DTA 20B and a TG 20. Infrared spectra were obtained with a Shimadzu IR-400 grating spectrophotometer using the nujol method and samples of 50 mg of the pyrolysis products of arbutin heated at $220\text{--}325^{\circ}\text{C}$ were used. For the trimethylsilylation [15–17] 30 mg of the pyrolysis products of arbutin at $220\text{--}325^{\circ}\text{C}$ were dissolved in 0.2 ml of pyridine. The solutions were trimethylsilylated with 0.25 ml of hexamethyldisilazane and 0.25 ml of trimethylchlorosilane. Gas chromatography was performed by injection of $1\ \mu\text{l}$ of the solution on a Shimadzu GC 4CPT equipped with TCD detectors and a stainless column (3 mm \times 3 m) packed with SE 30 silicon gum supported by Chromosorb W (80–100 mesh). The gas chromatographic peaks were characterized by specific retention time and area, and identified by comparison with authentic samples. Some pyrolysis products were quantitatively determined by mesoerythrite as an internal calibration standard. To evaluate the kinetics of the thermal decomposition of arbutin, thermogravimetric curves were recorded at heating rates of 0.5, 2, 5, 7.5 and $10^{\circ}\text{C min}^{-1}$. Arbutin was conserved in a desiccator heated at 80°C under reduced pressure, 10^{-3} mm Hg. All measurements in DTA and TG were carried out under atmosphere.

REACTION KINETICS

Many methods [22–28] of kinetic analysis have been proposed for the determination of kinetic parameters by use of thermogravimetric data. Two such methods are used and discussed to evaluate kinetic parameters.

Friedman's method [28] utilizes the following equation

$$(-1/w_0)(dw/dt) = A \exp(-E/RT) f(w/w_0) \quad (1)$$

where w_0 = weight of sample at time $t = t_0$, w = weight at t , A = pre-exponential factor, T = absolute temperature, R = gas constant, and E = activation energy.

Taking logarithms of eqn. (1) gives

$$\ln[(-1/w_0)(dw/dt)] = \ln[A f(w/w_0)] - E/RT \quad (2)$$

Plots of $\ln[(-1/w_0)(dw/dt)]$ against the reciprocal absolute temperature yield a straight line by the least squares method. The slope and the intercept

of the straight line are equal to $-E/R$ and $\ln[A f(w/w_0)]$, respectively. $f(w/w_0)$ is assumed as follows

$$f(w/w_0) = [(w - w_f)/w_0]^n \quad (3)$$

where w_f = weight of char and n = order of reaction.

Substituting eqn. (3) into eqn. (2) gives

$$\ln[A f(w/w_0)] = \ln A + n \ln[(w - w_f)/w_0] \quad (4)$$

An equation of a straight line of plots of $\ln A f(w/w_0)$ against $\ln[(w - w_f)/w_0]$ is determined by the least squares method. The order of reaction, n , and $\ln A$ are calculated from the slope and the intercept of the straight line, respectively.

Ozawa [22] has shown the following equation

$$\log \alpha = \log[(AE/I_n R) p(E/RT)] \quad (5)$$

where α = heating rate, $I_n = -\int dw/w^n$, and n = order of reaction. The approximation under the condition of $E/RT \geq 20$ has been carried out by Doyle [23]

$$\log p(E/RT) = -2.315 - 0.4567E/RT \quad (6)$$

Equation (5) gives

$$\log \alpha = \log(AE/I_n R) - 2.315 - 0.4567E/RT \quad (7)$$

Thermogravimetric curves are plotted at various heating rates against the reciprocal absolute temperatures. The logarithms of heating rates are then plotted against the reciprocal absolute temperatures for identical weight loss. Straight lines are determined by the least squares method. Activation energies are calculated from the slopes of the lines. The value of $\log I_n$ must be determined by plots of the weight changes against the values of $\log [(E/\alpha R) p(E/RT)]$, and $\log A$ is determined by subtracting the value of $\log [(E/\alpha R) p(E/RT)]$ from the value of $\log I_n$.

RESULTS AND DISCUSSION

The results of DTA and TG are shown in Fig. 1. The DTA curve of arbutin consists of three endothermic peaks at 205, 288 and 430°C, and two exothermic peaks at 388 and 540°C in the range room temperature to 550°C.

The thermogravimetric curve of arbutin shows that weight loss begins close to 200°C, is recorded as about 79% at 330°C, gradually decreases at a temperature higher than 330°C, and finally attains 0% at 550°C.

The results of paper chromatography in the pyrolysis products are as follows. The product heated at 220°C contains Hq and arbutin, the products at 240–260°C contain Hq, 16AGP, 16AGF and α - and β -D-glucose, the products at 270–290°C contain Hq, 16AGP and 16AGF, the product at 300°C contains Hq and 16AGP, the product at 320°C contains Hq only, and the products at a temperature higher than 330°C simply char.

The results of gas chromatography are shown in Fig. 2 and Table 1 by

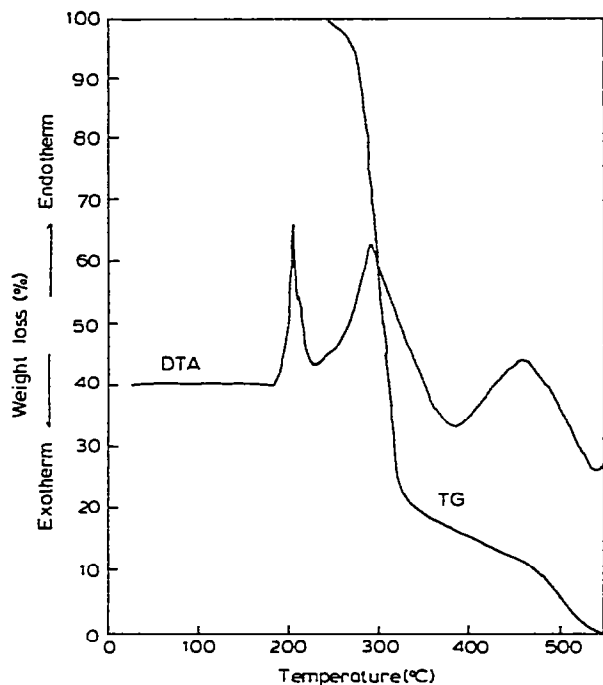


Fig. 1. DTA and TG curves of arbutin.

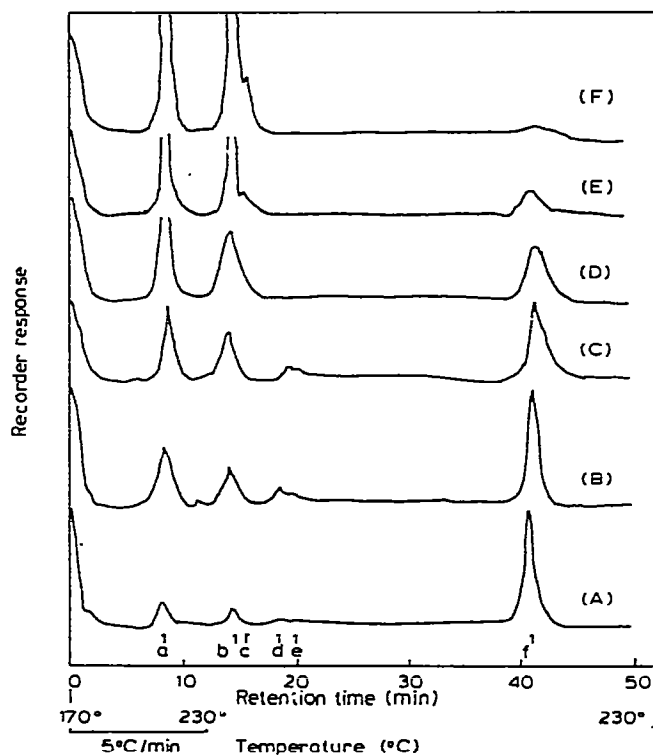


Fig. 2. Gas chromatograms of the pyrolysis products of arbutin which were trimethylsilylated. Pyrolysis temperature ($^{\circ}\text{C}$): (A) 240; (B) 250; (C) 260; (D) 270; (E) 280; (F) 290. a, Hydroquinone; b, 1,6-anhydro- β -D-glucopyranose; c, 1,6-anhydro- β -D-glucofuranose; d, α -D-glucose; e, β -D-glucose; f, arbutin.

TABLE 1

The thermal decomposition of 100 mg of arbutin at various temperatures

Heated temp. (°C)	Residue char (mg)	Tar (mg)	Pyrolysis products (mg) *					Arbutin (mg)
			Hq	16AGP	16AGF	α DG	β DG	
220								100
230								100
240		1.8	1.1	0.4		0.1		96.3
250		3.7	2.6	0.9		0.3		92.2
260		6.0	4.2	1.2		0.4	0.2	87.4
270		21.2	15.1	4.3		0.1	T	53.0
280	0.8	44.8	35.6	8.7	0.5	T	T	34.9
290	0.9	56.8	38.2	15.7	2.9	T	T	T
300	4.6	58.4	36.4	19.9	2.1			
320	12.3	48.6	28.5	5.1				
340	15.8	24.6						

* Hq, Hydroquinone; 16AGP, 1,6-anhydro- β -D-glucopyranose; 16AGF, 1,6-anhydro- β -D-glucofuranose; α DG, α -D-glucose; β DG, β -D-glucose. T = trace amounts.

using the pyrolysis products of arbutin heated at 220–340°C. The decomposition of arbutin takes place through a consecutively occurring reaction. The fate of the glycosyl moiety is detected by paper- and gas chromatography. Every stage of the pyrolysis reaction reflects decomposition of arbutin in accordance with elevating temperatures. Gas chromatographic analysis suggests that arbutin is detected from the pyrolysis products heated at 220–280°C and its thermal decomposition terminates at 280°C. The decomposition products are mainly Hq, 16AGP, 16AGF, α - and β -D-glucose. Hq is detected from the pyrolysis products at 230–320°C and involves 38.2 mg of the maximum value in the pyrolysis product at 290°C; 16AGP is also detected from the pyrolysis products at 240–320°C and 19.9 mg of the maximum value of it are involved in the pyrolysis product at 300°C; 16AGF is detected in the later stages of pyrolysis between 280 and 300°C, and 2.9 mg of the maximum value in the pyrolysis product at 290°C; α -D-glucose is 0.4 mg of the maximum value in the pyrolysis product at 260°C; β -D-glucose is 0.2 mg of the maximum value of the product at 260°C; and char remains in the pyrolysis products at 280–340°C.

Infrared spectra of the pyrolysis products of arbutin heated at 220–325°C are shown in Fig. 3 and these spectra are compared with each other. The band at 1710 cm^{-1} appears in the pyrolysis products at 300–320°C and is assigned to a C=O vibration [18]. The band at 1600 cm^{-1} corresponds to an aromatic nucleus [19] which is due to the aglycon 'hydroquinone' of arbutin. Its peak becomes smaller as the temperature increases from 220 to 300°C. Finally, the peak disappears in the pyrolysis product at 325°C. The band at 1205 cm^{-1} observed in the spectra of the pyrolysis products, except at 325°C, corresponds to a QH bending vibration [20,21]. The band at 1070 cm^{-1} in the spectrum of arbutin appears as a well-defined absorption peak and is due to a C=O stretching vibration [20]. This band also appears in the

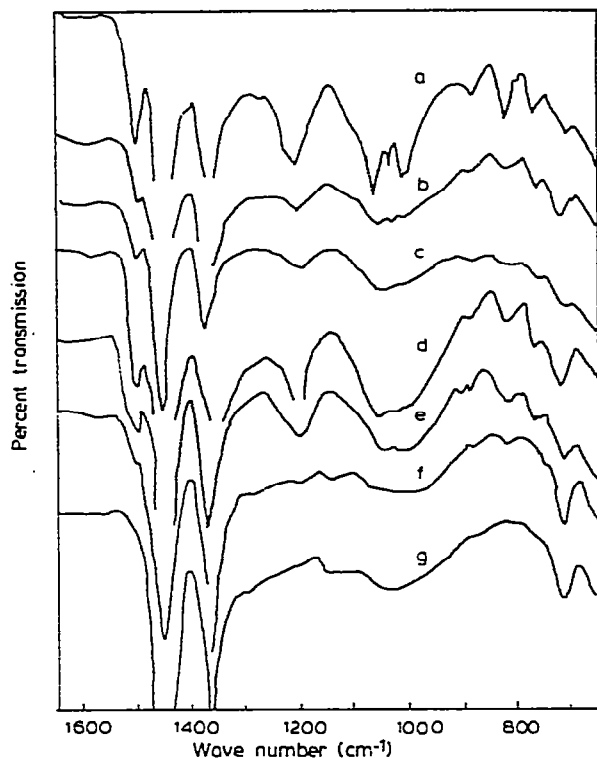


Fig. 3. IR spectra of the pyrolysis products of arbutin. Pyrolysis temperature ($^{\circ}\text{C}$): a, unheated; b, 220; c, 240; d, 260; e, 280; f, 300 $^{\circ}\text{C}$; g, 325.

spectra of the pyrolysis products at 220–280 $^{\circ}\text{C}$ and in the spectrum of arbutin, but disappears in the spectra of the pyrolysis products at temperatures higher than 300 $^{\circ}\text{C}$. As the thermal decomposition of arbutin progresses, the intensity of the band at 1070 cm^{-1} diminishes. The IR spectra results suggest that the thermal decomposition of arbutin terminates at 280 $^{\circ}\text{C}$.

Thermogravimetric curves are plotted at various heating rates against reciprocal absolute temperature, as shown in Fig. 4. Values of $\ln[(-1/w_0)(dw/dt)]$ are plotted against the reciprocal absolute temperatures in Fig. 5. Straight lines are drawn by the least squares method. The activation energies (average value, 26.27 kcal mole^{-1}) are calculated from the slopes which are equal to $-E/R$ and are shown in Fig. 6. The range of weight fraction, w/w_0 , is selected from zero to 0.30 because the IR spectra and gas chromatography data mentioned above suggest that arbutin remains at a temperature below 300 $^{\circ}\text{C}$. The values of $\ln[A f(w/w_0)]$ are also calculated by use of eqn. (4). The weight of w_0 is 50.0 mg and w_f , the weight of char, is 11.1 mg. Calculations based on plots of $\ln[A f(w/w_0)]$ against $\ln[(w - w_f)/w_0]$, as shown in Fig. 7, give $n = 0.985$, $\log A = 8.84$ and $A = 6.94 \times 10^8 \text{ sec}^{-1}$.

The logarithms of the heating rates are plotted against the reciprocal absolute temperatures for identical weight changes, as shown in Fig. 8. Straight lines are determined by the least squares method. The activation energy decreases from an initial value of 27.87 kcal mole^{-1} to a minimum value of 26.50 kcal mole^{-1} and then increases to an average value of 27.61

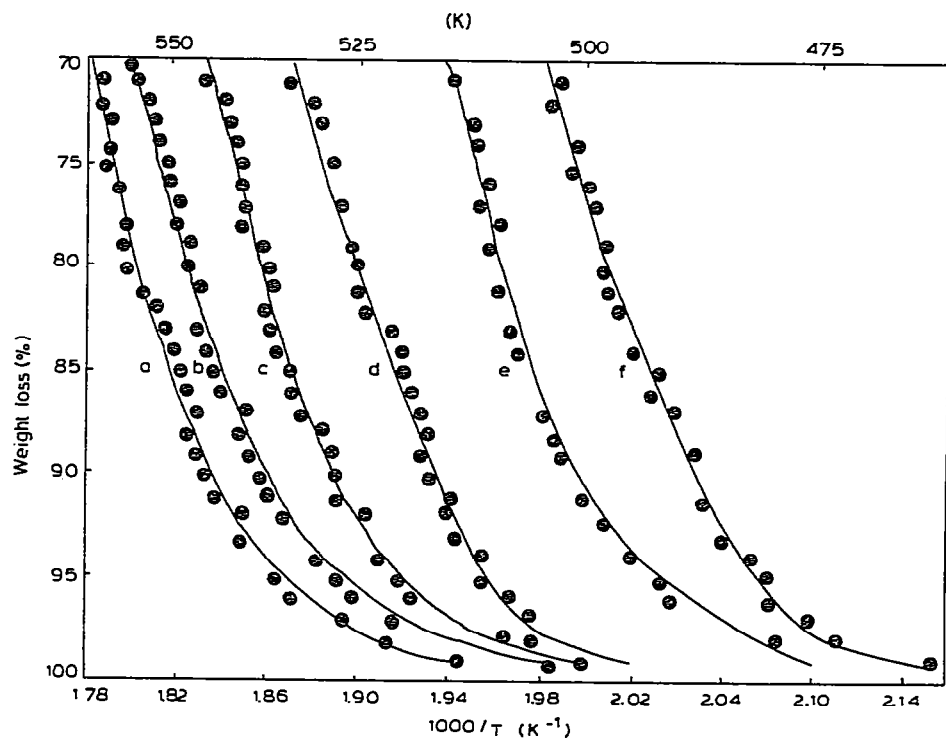


Fig. 4. The thermogravimetric curves of arbutin plotted against the reciprocal absolute temperature. Heating rate ($^{\circ}\text{C min}^{-1}$): a, 0.5; b, 1; c, 2; d, 5; e, 7.5; f, 10.

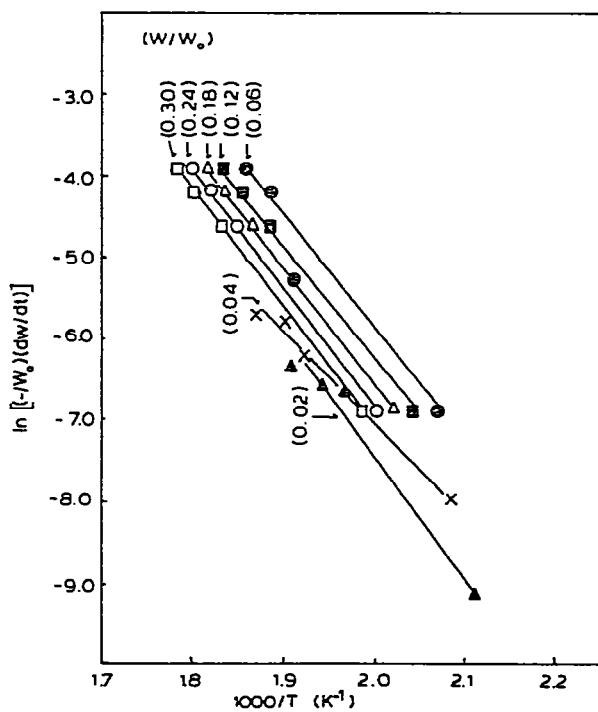


Fig. 5. Arrhenius type plots for determining kinetic parameters.

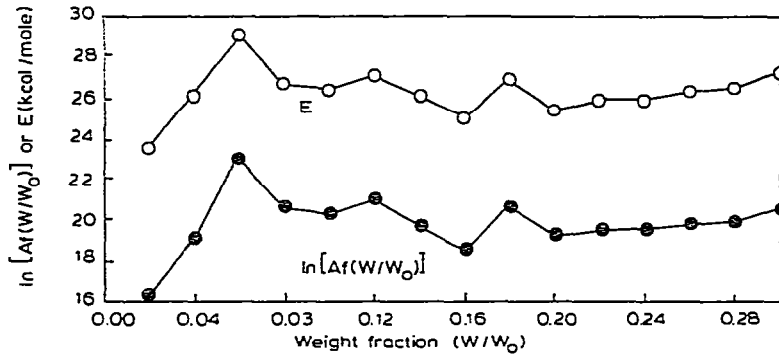


Fig. 6. Kinetic parameters as a function of weight fraction.

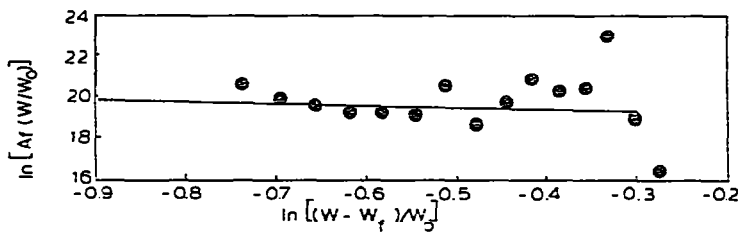


Fig. 7. Plots for the determination of $\ln A$ and order of reaction.

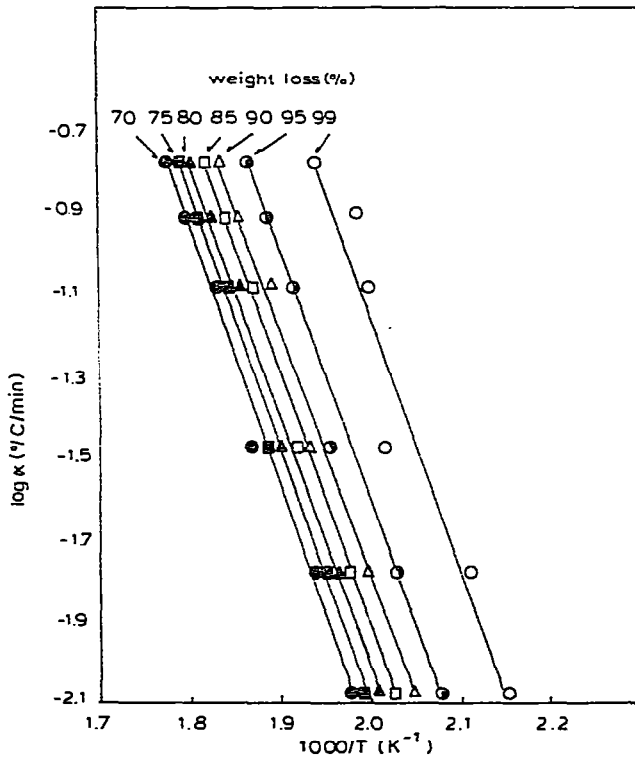


Fig. 8. Plots of logarithms of κ against reciprocal absolute temperatures.

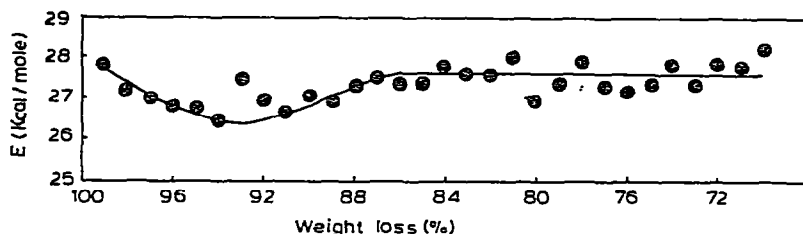


Fig. 9. Plots of activation energy against weight loss.

kcal mole⁻¹, as shown in Fig. 9. Doyle's approximation is discussed so that E/RT is larger than 20, i.e. $30.17 \geq E/RT \geq 25.40$. The weight changes are plotted against $\log [(E/RT) p(E/RT)]$ in Fig. 10. The mechanism of the thermal decomposition of arbutin can be interpreted as pseudo first order between 70 and 88% weight change. In the range 88–100% weight change, Friedman [28] suggested that early weight loss seemed to be accompanied by a different process [27], it was therefore decided to eliminate this portion from kinetic analysis. Consequently, $I_1 = -\int dw/w$ is obtained and accurate determination of $\log A$ can be calculated by the subtraction of $\log [(E/\alpha R) p(E/RT)]$ from $\log I_1$; $\log A = 8.19$ and $A = 1.55 \times 10^8 \text{ sec}^{-1}$.

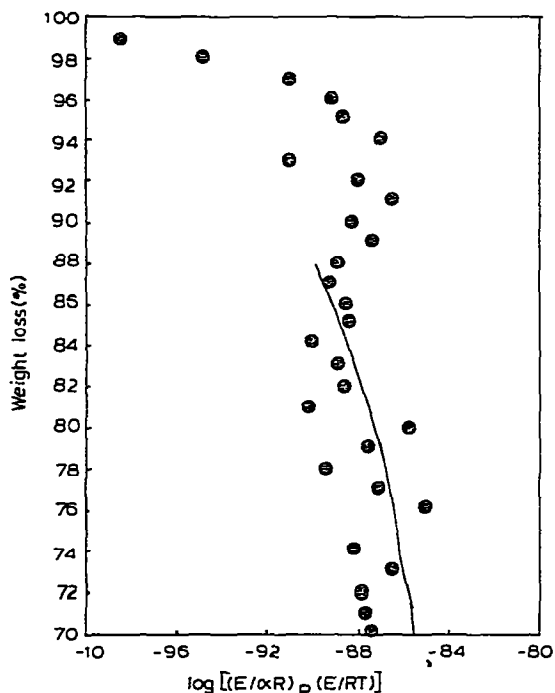


Fig. 10. Plots of the weight changes against $\log [(E/\alpha R) p(E/RT)]$.

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