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THE USE OF DYNAMIC THERMOGRAVIMETRY AND GAS CHROMATOGRAPHY TO THE STUDY OF THE CHEMICAL KINETICS OF SOLID-STATE DECOMPOSITION REACTIONS OF SOME SELECTED CRYSTALLINE AMINO ACIDS (AND COMPARISON OF THE METHOD OF DIFFERENTIAL THERMAL ANALYSIS)

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ABSTRACT

Dynamic thermogravimetry was used to the study of chemical kinetics of solid-state decomposition reactions of four selected crystalline amino acids, L-serine, L-lysine, L-phenylalanine, and L-cysteine. Gas chromatographic techniques were employed to the analysis of evolved gaseous products during the course of thermal degradation reactions. The determined kinetic parameters by dynamic thermogravimetry were compared to those evaluated by the method of differential thermal analysis from the literature. It was found that the dynamic thermogravimetry method provides a more rapid, sensitive, simpler, and direct means for determining the kinetic parameters than differential thermal analysis. The results of kinetic data were discussed briefly with the proposed chemical processes and the structural properties and thermal stability of the compounds.

INTRODUCTION

Thermoanalytical methods, such as dynamic thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC), for the determination of kinetic parameters from solid-state decomposition reactions have become universally popular since the last two decades. Several theoretical approaches to the derivation of kinetic parameters from TG data have been proposed and were reviewed and categorized quite completely by Flynn and Wall[1]. Kissinger[2, 3] presented a semitheoretical method for the evaluation of activation energy from multiple DTA runs based on the assumption that the temperature at the minimum, T_m, of the DTA peak coincides with the maximum reaction rate. However, there is only a few published literature concerning the comparative study of the use of both dynamic TG and DTA techniques to the determination of kinetic parameters of the solid-state decomposition

reaction. This report is therefore intended to provide a comparison of the experimentally determined kinetic parameters of thermal decomposition of some crystalline amino acids by the dynamic TG method with those available literature values estimated by the DTA approach.

In principle, each of the methods involves the following similar steps. (1) Combination of the rate equation or equations in question with the Arrhenius equation to eliminate the rate constant. (2) Transformation of the isothermal rate equation into dynamic form by substituting the temperature function for the time variable. (3) Conversion of the dynamic rate equation into experimentally applicable form through either approximation methods or exact solution techniques.

Among the many published dynamic TG methods, difference-differential method[4], integral method[5], and differential method[6], three methods have been comparatively studied and critically tested by several investigators[7-9]. The advantages of these methods are: (a) that only one TG curve for a single sample is required; (b) that the kinetic parameters can be evaluated over an entire temperature range in a continuous manner; (c) that dynamic techniques demand less time-consuming experiments than do the isothermal methods; (d) that a large amount of information is obtained without sample-to-sample error, since the same sample is used throughout the determination. These methods remain their potential applications in the analysis of reaction kinetics of solid-state decompositions.

Although Kissinger's approach for analyzing the kinetic data from DTA curves was criticized by Reed et al.[10] and Melling et al.[11] to be invalid in a practical experiment, Akita and Kase[12] have shown it to be valid provided that appropriate experimental conditions such as small cell dimensions, slow heating rate, and moderate reaction of sample materials are used. Akita and Kase[12] concluded that the peak minimum (i.e., T_m) of the DTA curve did agree with the maximum rate of reaction, in agreement with Kissinger, and placed the Kissinger relationship on a more sound theoretical basis.

Recently, Olafsson and Bryan[13-17] have adopted the Kissinger method to the determination of the "procedural activation energy", E_a, in terms of the T_m value and the heating rate, for thermal decomposition of crystalline amino acids. The procedure employed by these investigators are complicated in that (a) it required the determination of several DTA curves at different heating rates and (b) it needed a minimum of three Gaussians to be ressolved from the DTA curves by a sophisticated Curve Resolver. Thus, three similar or equivalent E_a values were generally obtained from three correspondingly resolved peaks of an original single endothermic peak of DTA curves. According to their reports, it seems that good linear relationships were observed for Kissinger's plots for most of the systems studied. Nevertheless, the results deserve to be justified.

It is the purpose of this paper to re-examine experimentally the thermal stability and decomposition kinetics of some selected crystalline amino acids in a more quantitative way by dynamic TG techniques. A simple, sensitive, graphical approximation method suggested by Broido[18] was employed to the analysis of kinetic data from

an entire temperature range of a single TG curve. A comparative study between the experimentally determined results and those values reported in the literature using Kissinger's treatment of DTA curves has been pursued and presented. The relationships of structure property–thermal stability–decomposition kinetics are attempted and discussed.

THEORETICAL

A simplified scheme for depicting the chemical change undergone by a solid substance during a thermal decomposition is:

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)} \tag{1}$$

where $A_{(s)}$ is the original solid reactant; $B_{(s)}$ is the solid residue which may or may not be present; and $C_{(g)}$ the gaseous product evolved.

At constant temperature, the rate expression for kinetic analysis based on the change in mass or weight of $A_{(s)}$ follows a model equation as:

$$\left[\frac{dX_t}{dt}\right]_T = k_T(1 - X_t)^n \tag{2}$$

where X_t is the fraction of material decomposed at time, t; $(dX_t/dt)_T$ is the instantaneous decomposition rate; k_T is the temperature dependence of the Arrhenius rate constant; n is the order of reaction.

For a first-order thermal decomposition reaction and assuming the rate constant k_T changes with absolute temperature according to the Arrhenius equation:

$$k_T = A \exp^{-E_a/RT} \tag{3}$$

where R is the universal gas constant; T is the absolute temperature; E_a is the activation energy, and is often interpreted as the energy barrier opposing the reaction; and A is a pre-exponential factor, often called the frequency factor, is a measure of the probability that a molecule having energy E_a will participate in a reaction.

By substituting eqn (3) into eqn (2), one obtains a generalized equation in the form:

$$\frac{dX_t}{dt} = A(1 - X_t) \exp^{-E_a/RT} \tag{4}$$

which holds for any value of T, whether constant or variable, so long as X_t and T are measured at the same instant.

Almost all mathematical derivations for kinetic analysis are based upon eqn (4). In this paper, only Kissinger's approach for DTA curve analysis and Broido's approximation method for dynamic TG curve treatment are briefly reviewed. In addition, the appropriate consideration of Kissinger relationships by Akita and Kase is also presented.

Kissinger's approach for DTA curve analysis

If the experiment is carried out dynamically so that the temperature, T, is a linear function of time, t, i.e.,

$$T = T_0 + \phi t \tag{5}$$

and the heating rate, ϕ, is defined as:

$$\frac{dT}{dt} = \phi \tag{6}$$

Further, by differentiating eqn (4) with respect to time, t, eqn (7) is obtained.

$$\frac{d}{dt}\left(\frac{dX_t}{dt}\right) = \frac{dX_t}{dt}\left[\frac{E_a}{RT^2}\left(\frac{dT}{dt}\right) - A\exp^{-E_a/RT}\right] \tag{7}$$

When the reaction rate is a maximum, the derivative, $(d/dt)(dX_t/dt)$, with respect to time is zero. Besides, the maximum value of dX_t/dt occurs at temperature T_m, therefore, eqn (7) becomes

$$A\exp^{-E_a/RT_m} = \frac{E_a}{RT_m^2}\phi \tag{8}$$

By taking natural logarithms of eqn (8), the Kissinger equation is yielded:

$$\ln\left(\frac{\phi}{T_m^2}\right) = -\frac{E_a}{R}\left(\frac{1}{T_m}\right) + \ln\frac{AR}{E_a} \tag{9}$$

Hence, a plot of $\ln(\phi/T_m^2)$ against $1/T_m$ should produce a straight line with a slope equal to $-E_a/R$ and the Y-intercept equal to $\ln(AR/E_a)$. Thus, E_a and A, in turn, can be determined simultaneously. Such a plot has been used extensively by Olafsson and Bryan[13-17] for obtaining kinetic parameters of amino acids decomposition from DTA curves.

Verification of Kissinger's approach by Akita and Kase

Akita and Kase[12] derived basic equations of DTA for the infinite cylindrical sample with first-order reaction and solved the differential equations strictly by Laplace transformation and Green's function method. With some assumptions and approximations, they presented the final simplified form of equation (eqn (38) in ref. 12) as

$$\Delta T = \frac{a^2 - r^2}{4}\left\{\left(\frac{1}{k_1} - \frac{1}{k_2}\right)\phi + \frac{1}{k_2}\frac{Q\,w_0}{c_2 w_2}\left[\frac{d}{dt}\left(\frac{w}{w_0}\right)\right]\right\} \tag{10}$$

where a is the radius; r is the radial coordinate; k_1 and k_2 are the mean thermal diffusivities of materials packed in each cell; Q is the heat of reaction per weight; c_2 is the mean specific heat of the sample cell; w_2 is the total weight of sample cell; w_0 is the initial weight of reactant; and $d(w/w_0)/dt$ is the reaction rate of the reactant.

Eqn (10) means that the temperature difference in DTA has a linear correlation with the reaction rate. On the other hand, eqn (39) of their article[12],

$$\frac{\mathrm{d}}{\mathrm{d}t}(\Delta T) \cong \frac{a^2 - r^2}{4k_2} \frac{Q w_0}{c_2 w_2} \left[\frac{\mathrm{d}^2}{\mathrm{d}t^2} \left(\frac{w}{w_0} \right) \right] \tag{11}$$

shows that the peak of the DTA curve just coincides with the inflection point of the TG curve. These equations support the theory of Kissinger within certain limits of the experimental conditions, such as heating rate, the cell size, and the kinetic properties of the sample material.

Broido's approximation method for dynamic TG curve treatment

Broido stated that W_t, the weight at any time, t, is related to the fraction of the number of initial molecules not yet decomposed, y, by the equation

$$y = \frac{N}{N_0} = \frac{(W_t - W_\infty)}{(W_0 - W_\infty)} \tag{12}$$

where W_0 is the initial weight of reacting material, W_∞ is the weight of final residue (which is equal to zero for a complete decomposition).

By substituting eqn (6) and eqn (12) into eqn (4) and rearranging, a differential form of rate equation was obtained:

$$\frac{\mathrm{d}y}{y} = -\left(\frac{A}{\phi}\right) \exp^{-E_a/RT} \mathrm{d}T \tag{13}$$

In order to integrate the right-hand side of eqn (13), Broido used one of the alternate assumptions,

$$\exp^{-E_a/RT} \cong (T_m/T)^2 \exp^{-E_a/RT} \tag{14}$$

which was suggested by Horowitz and Metzger[19]. The assumption was based on the statement given by Van Krevelen et al.[20] that almost the entire measurable reaction usually occurs within $\pm 10\%$ of T_m, the temperature of maximum reaction velocity.

After integration of both sides of eqn (13) and taking logarithm of the resulting equation, a simplified final form of Broido's equation was obtained:

$$\ln \ln \left(\frac{1}{y}\right) = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \text{constant} \tag{15}$$

where constant $= \ln (ART_m^2/\phi E_a)$

Eqn (15) indicates that if the plot of $\ln \ln (1/y)$ versus $(1/T)$ is linear, the decomposition reaction (including many pyrolysis reactions) is a first-order reaction. Thus, E_a can be calculated from the slope, and the pre-exponential factor A evaluated from the Y-intercept constant. This equation is very sensitive to the effects of sample and instrumental factors. It has been tested by Boido and shown to give an excellent approximation to a straight line over the range $0.999 > y > 0.001$.

Modification of Broido's method for treating experimental data

Since, in practical dynamic TG experiment, instead of weighing the sample at any time, t, the TG curve actually monitoring the continuous change (or decrease) in the weight of a sample as function of time and temperature, eqn (15) is thus further modified for treating the experimental data. That is,

$$\frac{1}{y} = \frac{1}{\dfrac{(W_t - W_\infty)}{(W_0 - W_\infty)}} = \frac{(W_0 - W_\infty)}{(W_t - W_\infty)} = \frac{(W_0 - W_\infty)}{(W_0 - W_\infty) - (W_0 - W_t)}$$

$$= \frac{\Delta W_{total}}{(\Delta W_{total} - \Delta W_t)} = Z \tag{16}$$

where ΔW_{total} = total change in weight of a sample after completion of decomposition, and ΔW_t = change in weight of active material at time, t. With such modification, eqn (15) can be rewritten as

$$\ln \ln (Z) = -\left(\frac{E_a}{R}\right)\left(\frac{1}{T}\right) + \ln (ART_m^2/\phi E_a) \tag{17}$$

Eqns (15) and (17) have been successfully applied to the determination of kinetic parameters of the desorption of liquid solvents from polymeric membranes[21, 22] and of the thermal degradation of polymeric materials[23, 24]. In the present study, eqn (17) has been adequately used in the analysis of TG curves for obtaining kinetic data for amino acid decomposition.

EXPERIMENTAL

Methods and equipments

A dynamic (non-isothermal) TG technique was used in the kinetic study of decomposition reaction experiments. The Fisher Series 100 TG system (manufactured by Fisher Scientific Co., Pittsburgh, PA) was employed in all TG experiments. This system consists of Model 120P TG accessory, Model 360 linear temperature programmer, Model 260F furnace, Cahn RG electrobalance (manufactured by Cahn Instrument Co., Paramount, CA), and two-channel "Servo/Riter II", 1-mV strip chart Recorder (Texas Instruments, Inc., Houston, TX).

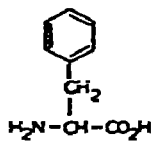
Procedure

Four standard crystalline amino acids were examined in this study. These compounds are L-serine, L-lysine, L-phenylalanine, and L-cysteine. They were all in the form of free acids and were of the highest purity obtained commercially (Sigma Chemical Co., St. Louis, MO). Table 1 lists the compounds and summarizes a number of physical properties for each compound.

For decomposition study under dynamic condition the TG instruments were set up as follows: Sample size: 2.00 ± 0.01 mg; electrobalance sensitivity: 0.01 mg;

TABLE 1

SOME PHYSICAL PROPERTIES OF AMINO ACIDS[a]

Compound	*Classification*	*Molecular weight*	*Molecular structure*	pK_a	p*I*	*Melting point*[b] (°C)
L-Serine (Ser)	Hydroxyamino acids	105.1	CH_2OH $H_2N-CH-CO_2H$	2.21 9.15	5.68	228
L-Lysine (Lys)	Amino acids having basic functions	146.2	$(CH_2)_4-NH_2$ $H_2N-CH-CO_2H$	2.18 8.95(α) 10.53(ε)	9.74	224–225
L-Phenylalanine (Phe)	Aromatic amino acids	165.2		1.83 9.12	5.98	284
L-Cysteine (Cys)	Sulfur-containing amino acids	121.2	CH_2SH $H_2N-CH-CO_2H$	1.71 8.33 (sulfhydryl) 10.78(α)	5.02	178

[a] From R. Mahler and E. H. Cordes, *Biological Chemistry*, Harper & Row, New York, 2nd. ed., pp. 44–47.

[b] From H. A. Sober (Ed.), *Handbook of Biochemistry*, The Chemical Rubber Co., Cleveland, Ohio, 44128 2nd. ed., 1970.

recorder span: 2 mg full scale; heating rate: in increasing rate of 10°C min^{-1}; recorder chart speed: 0.5 in. min^{-1}; inert gas atmosphere: flushing with helium gas at a constant flow rate of 200 ml min^{-1}; operation temperature range: ambient temperature to the completion of decomposition. A schematic diagram of the experimental set-up is shown elsewhere[21].

In order to avoid the oxidative decomposition of the sample, the TG-sample system was first evacuated and then flushed with helium at a flow-rate of 500 ml min^{-1} before starting the non-isothermal TG run. While, a constant flow-rate of 200 ml min^{-1} of helium was continuously flushed to remove the evolved gases during the pyrolytic decomposition experiment. At least duplicate runs for each compound were made. These weight changes as a function of temperature (and time), TG curves, were used in the determination of kinetic data. Several points were taken from the original TG curves, converted to log log (z), and plotted against the reciprocal absolute temperature ($1/T$) utilizing eqn (17). All calculations were made by the method of least squares with a computer and Fortran IV language. The activation energies and the pre-exponential factors were then evaluated from the linear plots of eqn (17) simultaneously.

The derivative thermogravimetric experiments (DTG) were carried out simultaneously with TG runs by setting a full scale of 1 mg min^{-1} and sensitivity of 0.01 mg. From the DTG curves, the temperatures of the maximum thermal degradation were evaluated accordingly (i.e., $T_{max.}$).

The decomposed gaseous products in the TG systems were measured with a Beckman GC-2A gas chromatograph equipped with a thermal conductivity detector and a 6-ft. stainless-steel column packed with molecular sieve 5A. Another 6-ft. stainless-steel column packed with Porapak Q was used to determine ammonia (NH_3) and carbon dioxide (CO_2) gases evolved during the thermal degradation processes. Helium was used as a carrier gas. The column temperature used was 70°C. The sample size of gases injected into the column was 1 cc (or ml) using a Hamilton syringe. A standard calibration method was employed in all gas determinations. For each amino acid studied, the measurement of evolved gases was made at several time and temperature intervals. Only several significant gases which are directly related to the study of thermal degradation kinetics are reported and discussed here, however.

RESULTS AND DISCUSSION

A typical simultaneous TG–DTG curves showing the plots of percent weight remaining as a function of temperature obtained from the original degradation curve for L-phenylalanine (Phe) is presented in Fig. 1. From these curves, a considerable

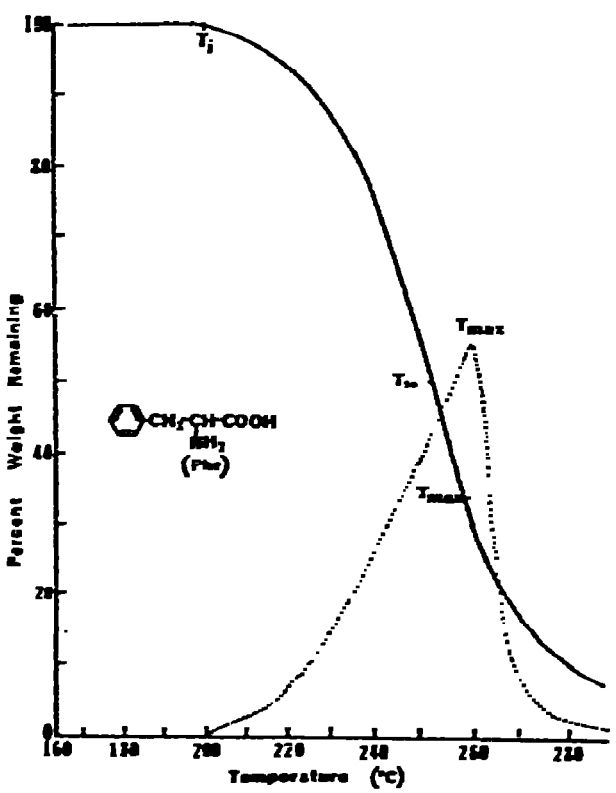


Fig. 1. A typical simultaneous TG–DTG curve showing the thermal degradation of L-phenylalanine (L-Phe) as a function of temperature.

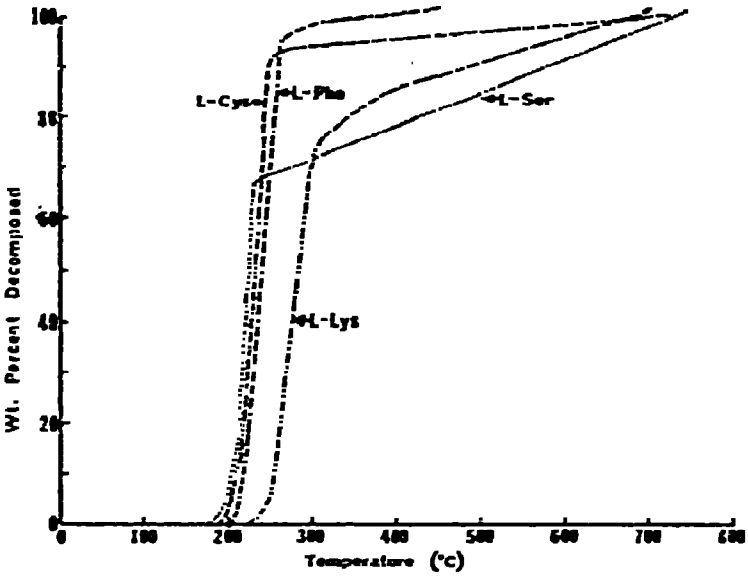


Fig. 2. Thermogravimetric analysis curves for L-serine (L-Ser), L-lysine (L-Lys), L-phenylalanine (L-Phe), and L-cysteine (L-Cys).

TABLE 2

THERMAL STABILITY OF SELECTED AMINO ACIDS

Compound	*Temperature at specific weight percent of degradation (°C)*						*Temperature at maximum rate of degradation (°C)*	
	T_i	T_{10}	T_{25}	T_{50}	T_{75}	T_f	$T_{max.}$ *(DTG)*	$T_{max.}$ *(DTA)*[a]
L-Serine	182.5	206.5	217.6	221.8	370.0	733.5	224.9	232.0
L-Lysine	231.2	259.0	268.4	284.2	318.4	592.3	268.4	233.0
L-Phenyl-alanine	202.8	221.8	233.5	244.0	253.7	439.3	257.0	276.0
L-Cysteine	186.0	210.0	219.5	225.3	228.8	688.7	227.2	231.0

[a] From ref. 14 by DTA techniques.

amount of information such as the temperature of initiation of degradation (T_i), temperatures at the specified weight percent of degradation T_{10} (10%), T_{25} (25%), T_{50} (50%), and T_{75} (75%), and the temperatures at the maximum rate of degradation ($T_{max.}$) and the completion of degradation (T_f), and the kinetic parameters, and so on were evaluated. The simultaneous TG–DTG curves for L-serine (Ser), L-lysine (Lys), and L-cysteine (Cys) showed similar thermal degradation patterns to those of Phe and are consequently not given. Instead, the detailed degradation pictures in terms of weight percent decomposed as a function of temperatures for all four compounds are shown in Fig. 2. These curves clearly indicate that, for structurally different amino acids, their thermal behavior is also not identical. The further analyzed

numerical data, which may be utilized to represent the thermal stability of the amino acids selected, will clarify the implication of this statement (Table 2). From comparisons of these thermal data (Table 2) with some physical properties tabulated in Table 1, it is quite obvious that Ser, a hydroxyamino acid, and Cys, a sulfur-containing amino acid, with smaller molecular weights and lower melting points, are initially less stable (T_i = 182.5°C for Ser and 186.0°C for Cys) and finally more resistant to thermal effect (T_f = 733.5°C for Ser and 688.7°C for Cys) than the other two, Lys (T_i = 231.2°C, T_f = 592.3°C), an amino acid having basic function, and Phe (T_i = 202.8°C, T_f = 439.3°C), an aromatic amino acid. Both $T_{max.}$ data obtained from DTG and DTA methods are very comparable and exhibited similar trends of thermal effects for four compounds. However, it should be pointed out that $T_{max.}$ for Lys determined by DTG (268.4°C) is about 35°C higher than that by DTA (233.0°C). On the contrary, it is about 19°C lower for Phe by DTG (257.0°C) than by DTA (276.0°C). It appears, probably, that the reaction atmospheres and the decomposition mechanisms play effective roles in these cases. It is generally recognized that the values of $T_{max.}$ obtained by the DTG method are more reproducible and reliable than those evaluated from DTA curves[25]. This is due to the fact that the DTG measurements indicate exactly the temperatures of the maximum reaction rate with the first derivative of the mass-change with respect to time, dm/dt, occurring at $T_{max.}$, while the curves for DTA extend over a wider temperature interval, owing to subsequent warming of the material after the reaction. Furthermore, with the excep-

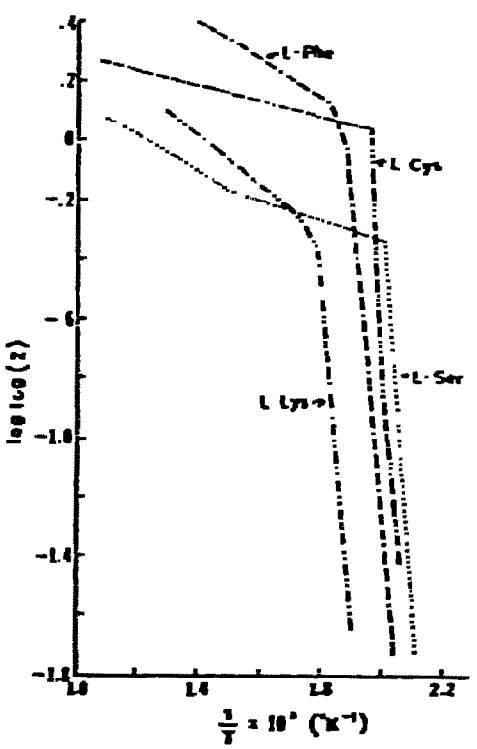


Fig. 3. Plots of log log (Z) vs. $1/T$ for L-Ser, L-Lys, L-Phe, and L-Cys for evaluation of kinetic parameters of solid-state decomposition reaction.

TABLE 3

KINETIC PARAMETERS OF THERMAL DEGRADATION OF AMINO ACIDS

Compound	*Kinetic parameters*											
	First stage of degradation				*Second stage of degradation*				*Third stage of degradation*			
	E_{a_1} (*kcal mol*$^{-1}$)	ΔW_1 (%)	ΔT_1 (°C)	*log* A_1	E_{a_2} (*kcal mol*$^{-1}$)	ΔW_2 (%)	ΔT_2 (°C)	*log* A_2	E_{a_3} (*kcal mol*$^{-1}$)	ΔW_3 (%)	ΔT_3 (°C)	*log* A_3
L-Serine	53.76 (57.5)[a]	74.9	182.5–226.7	23.590	1.14	8.2	226.7–310.5	−1.093	3.11	15.6	310.5–495.6	0.119
L-Lysine	53.59 (56.5)[a]	54.6	231.2–286.7	20.901	7.96	20.9	286.7–318.4	2.193	3.68	15.9	318.4–462.6	0.255
L-Phenylalanine	50.09 (53.0)[a]	55.0	202.8–245.0	20.987	16.71	39.5	245.0–273.0	6.649	2.79	4.7	273.0–390.0	0.317
L-Cysteine	39.80 (36.0)[a]	12.0	186.0–210.0	17.319	71.02	79.2	210.0–230.0	31.288	1.63	6.7	230.0–306.0	−0.353

[a] From ref. 16 by DTA techniques.

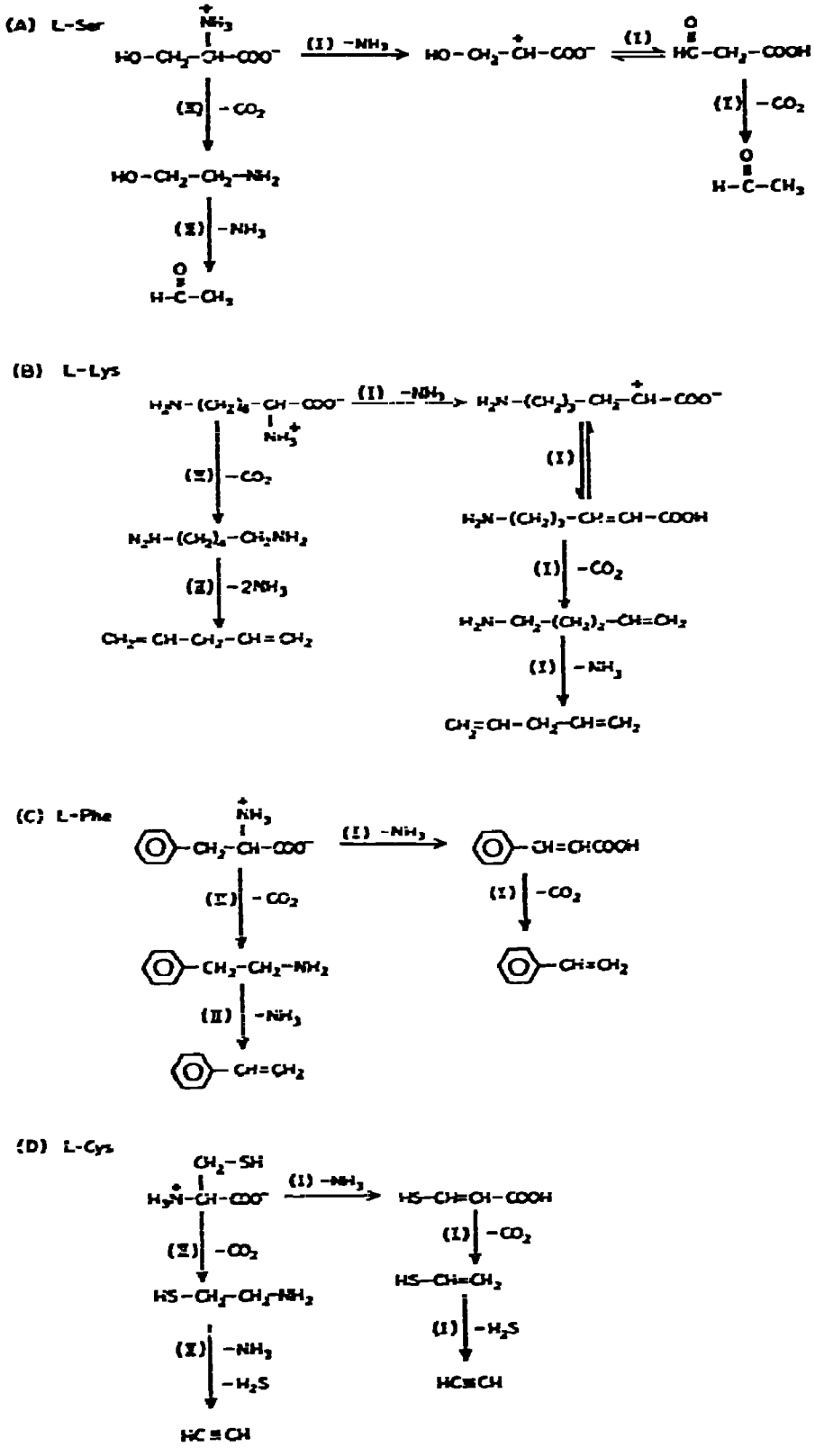


Fig. 4. Sequences of chemical processes for thermal degradation of (A): L-Ser; (B): L-Lys; (C): L-Phe; (D): L-Cys.

tion of Ser the T_{max} measured either by DTG or DTA techniques did not correspond to the melting point (m.p.) of the compounds studied. The maximum reaction rate of Phe occurred before the normal melting behavior while those of Lys and Cys took place way beyond the m.p. Therefore, it is impossible to predict the thermal behavior of these amino acids from the available ordinary physical properties with acceptable accuracy.

Figure 3 shows the kinetic profiles for Ser, Lys, Phe, and Cys. As can be seen, the plots of log log (Z) vs. $1/T$ over the entire range of decomposition reactions from the original TG curves (Figs. 1 and 2) provide an extremely sensitive method of detecting small deviations in an otherwise simple, unique pyrolysis reaction. For each compound, three distinguishable linear portions of plots indicating three separating component reactions in the overall complicated pyrolysis process are observed. This demonstrates that the extreme sensitivity of such plots to minute changes could be utilized to obtain a linear relationship over a short range corresponding to a separated-single, first-order Arrhenius-type of component reactions. In other words, it also means that the estimated component kinetic parameters for each compound is highly indicative of different reaction mechanisms involved in the entire decomposition reaction. Thus, three sets of activation energies designated as E_{a_1}, E_{a_2}, and E_{a_3} and three sets of pre-exponential factors as log A_1, log A_2, and log A_3, respectively, were evaluated from those linear plots shown in Fig. 3 and are listed in Table 3. In this table, both the ranges of weight and temperature changes corresponding to each stage of degradation are also tabulated. With the exception of Cys, the reported E_{a_1} values for the first stage of degradation by the DTA method[16] are about 5% higher than those experimentally determined by the TG techniques (for Cys, it is 10% lower). As mentioned previously, this could be interpreted as resulting from the thermal effects in the different reaction atmospheres of the DTA method as for T_{max} values. These values are mainly the procedural activation energies for the chemical processes of the component decomposition reactions of deamination, and deamination followed by decarboxylation. The detailed reaction sequences are shown in Fig. 4.

For Ser, Lys, and Phe, these results of reaction series are in agreement with those proposed by other workers[15, 17, 25]. The percent weight loss (ΔW_1) estimated by the TG technique and the evolved gas analysis for NH_3 and CO_2 by GC strongly support these decomposition reaction mechanisms occurring in the lower temperature range of 180 to 290°C. For example, the values of ΔW_1 for Ser, Lys, and Phe are 74.9, 54.6, and 55.0%, while the calculated percent weight loss due to the evolving of NH_3, NH_3 plus CO_2 gases are 74.2, 53.3, and 47.2%, respectively. As for Cys, which is a sulfur-containing amino acid, the computed E_{a_1} value is essential for the deamination process at the temperature range of 186 to 210°C since the calculated weight percent loss for NH_3 from GC analysis is 14.0% and that for ΔW_1 from TG is 12.0% (Table 3). However, in the temperature range of 210 to 230°C the higher E_{a_2} values for the second stage of degradation demonstrate the activation energies required for the deamination (a continuation process), decarboxylation and dehydrosulfidation processes. The estimated weight percent loss due to the evolved gases of NH_3, CO_2,

and H_2S from GC is 78.4%, while that from TG is 79.2% (ΔW_2). The reaction sequences are shown in Fig. 4.

The E_{a_2} and E_{a_3} values for the second and third stages of degradation are only 1.14 and 3.11 kcal mol^{-1}, respectively, for Ser. These quantities are just the activation energies necessary for the slow dehydrogenation reaction from the residual products in the higher and longer temperature range (227 to 500°C). The total weight percent loss is only 24% ($\Delta W_2 + \Delta W_3$). Possibly, it also involves the dehydration and demethylation processes since H_2, CH_4, and H_2O (trace) were also found in the residual product chamber by GC.

The weight percent change (ΔW_2) for the second stage of degradation of Lys is 20.9%. This change requires about 8 kcal mol^{-1} of energy to induce the reaction within a short range of temperature change (286.7 to 318.4°C). It may be interpreted as indicating that the continuous deamination of the -amino group and the dehydrogenation and demethylation processes occurred simultaneously in this stage. The values of E_{a_3} and ΔW_3 for the third stage of degradation of Lys are very close to those values of Ser at the same stage, and therefore, the decomposition processes could be interpreted similarly to those for Ser. (For Ser: E_{a_3} = 3.11 kcal mol^{-1}, ΔW_3 = 15.6%; Lys: E_{a_3} = 3.68 kcal mol^{-1}, ΔW_3 = 15.9%).

The activation energies for the second stage of degradation of Phe (E_{a_2}) is 16.71 kcal mol^{-1}. The weight percent change (ΔW_2) for this stage is 39.5%. It is interesting to note that this change occurred at the short temperature range of $T_{max.} \doteq 14.0$°C (i.e., $T_{max.}$ = 257.0°C, ΔT_2 — 245.0 to 273.0°C). GC analysis of the degradation mixture indicates a larger amount of NH_3 and CO_2, and trace of CO gases. After this stage, Phe completed the degradation at 390°C with a residual weight loss of 4.7% (ΔW_3) and only took up 2.79 kcal mol^{-1} of energy (E_{a_3}) for dehydrogenation and demethylation processes.

A direct check of the functional relationship between A (frequency factor in terms of log A) and E_a (activation energies for all stages of degradation, E_{a_1}, E_{a_2}, E_{a_3},

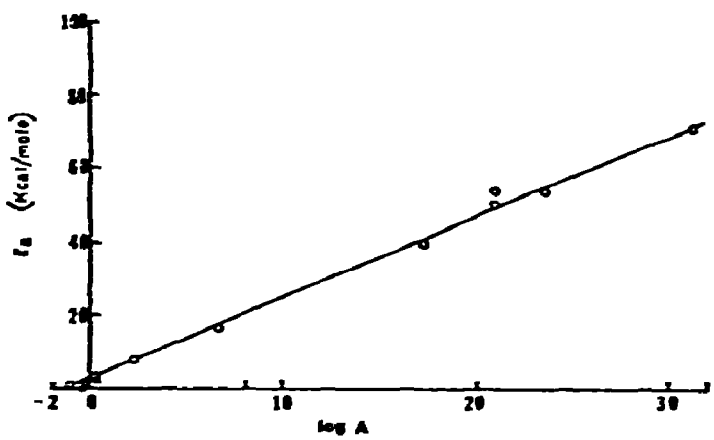


Fig. 5. Relationship between E_a and log A obtained at three different stages of thermal degradation of L-Ser, L-Lys, L-Phe, and L-Cys.

etc., from Table 3) is shown in Fig. 5. As is expected, a linear relationship is observed. This relationship can be expressed in the form

$$E_a = 3.34\ (\text{kcal mol}^{-1}) + 2.24\ (\text{kcal mol}^{-1}) \times \log A \qquad (18\text{-A})$$

or

$$\log A = -1.49 + 0.45 \times \frac{E_a}{(\text{kcal mol}^{-1})} \qquad (18\text{-B})$$

Thus one can estimate E_a value for the desired component reaction with known value of A at the specified T_{max}, or temperature range, ΔT, and vice versa. With a 95% confidence, the correlation coefficient is 0.995.

In conclusion, the kinetic parameters of thermal degradation of amino acids determined by the TG techniques utilizing Broido's approximation method are very comparable to those evaluated by the DTA method using Kissinger's approach. This is particularly true for the first stage of degradation by TG, which could be considered as the main component reaction during the overall reaction. However, it is evident that the TG techniques offer more direct, rapid, and simpler measurement of rate processes of the separated component reactions from a complex system composed of several first-order component reactions than the DTA method. TG can measure the overall rate of disappearance of reactants which follow a solid-gas type of process (eqn (1)) and a rate expression (eqn (2)), and then evaluate the kinetic parameters for any portion of weight changes corresponding to the first-order component reactions within the specified temperature ranges. While, the success of measuring kinetic parameters by the DTA method using Kissinger's approach was dependent on the validity of the T_{max} values derived from the series of resolved DTA curves obtained (from the complicated curve-fitting processes by a computer) at different heating rates (from the separated different sets of experiments)[15] and on the limits of the experimental conditions mentioned previously. It is found from this study that the TG techniques and GC method provide more suitable means for the determination of kinetic parameters and mechanisms of thermal degradation of crystalline amino acids. Of course, the most effective and powerful techniques in this aspect would be, if it was possible to use a direct combination of TG–GC–MS (mass spectrometry) tools.

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