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THERMOVOLTAIC DETECTION. III. THERMAL DECOMPOSITION OF SOME AMINO ACIDS *

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ABSTRACT

The thermal dissociation reactions of selected amino acids were studied by thermovoltaic detection (TVD), TG and DSC. All of the TVD curves except L-arginine contained a broad EMF output peak in the 200–300°C temperature range. The leading edges of the peak maxima were reproducible to within ±1–2% while the trailing edges were reproducible to ±20% or so. The latter was related to the irreproducible nature of the electrode-decomposition products interface. The TVD curves were not unique in that they yielded thermal analysis curves that were not inherently different from other TA techniques.

INTRODUCTION

The thermal analysis technique of thermovoltaic detection (TVD), as discussed previously [1,2], records the EMF (in volts) generated by a thermal decomposition or phase change reaction (solid → liquid) as a function of sample or furnace temperature. An EMF is generated as a result of the reaction of the sample with two dissimilar electrodes, usually aluminum and platinum metals. The TVD technique has been applied to the study of many diverse substances such as metal salt hydrates, transition metal coordination compounds, polymers, organic compounds, coal, clays and others.

In this investigation, TVD is used to study the thermal behavior of compounds of biological interest, the amino acids. The thermal properties of amino acids in the crystalline state has been the subject of numerous studies, especially the polymerization and condensation reactions under conditions believed to have been prevalent on primordial earth. Olafsson and Bryan [3–6] have used DSC along with curve resolving techniques to show that many amino acids thermally dissociate by up to three different steps. They determined the thermal stability of these reactions as well as the activation energy, E_a, for their kinetics using Kissinger's method [7].

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Since the thermal decomposition reactions of amino acids are fairly well known and possess a moderate degree of complexity, it was of interest to apply the TVD technique to the study of these compounds.

EXPERIMENTAL

TVD apparatus

The TVD apparatus was similar to Apparatus II previously described [2]. The spring loaded electrode system was replaced by a weight loaded (200 g) configuration which permitted more uniform and reproducible sample–electrode loading and hence more reproducible TVD curves. Sample sizes were quite small, usually 1.5–2.0 mg. A furnace heating rate of 10°C min^{-1} was employed, to a maximum temperature of about 400°C.

DSC apparatus

The DSC curves of the amino acids were obtained on an Omnitherm system under the same conditions as the TVD studies.

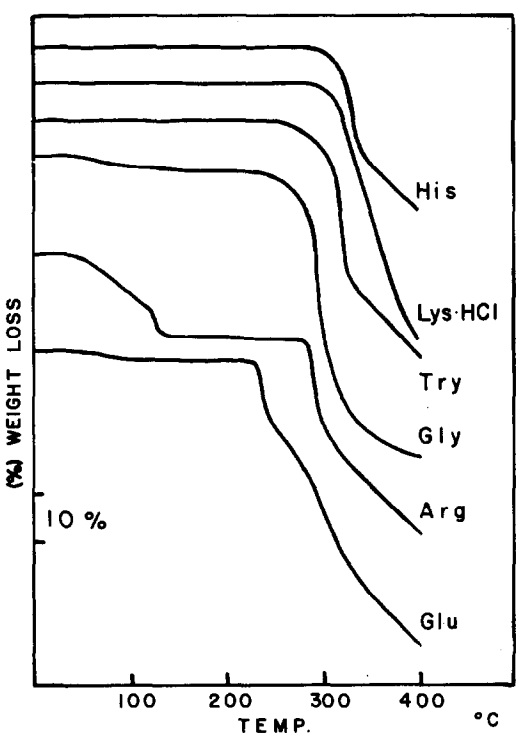

Fig. 1. TG curves of selected amino acids.

TG apparatus

The TG curves of the amino acids were obtained on a Perkin–Elmer Model TGS-2 system under the same conditions as the TVD studies.

Amino acids

The amino acids were commercially available samples obtained from the Aldrich Chemical Co., Eastman-Kodak Co., and Nutritional Biochemical Corp.

RESULTS AND DISCUSSION

The TG curves of the amino acids studied in this investigation are illustrated in Fig. 1.

All of the compounds, except L-arginine, have a single-step decomposition TG curve which ended with a black, carbonaceous residue (in nitrogen). L-Arginine contained water of hydration which is evolved in the 100–150°C temperature range. The anhydrous acid then dissociates, beginning at about 280°C. All of the other amino acids begin to decompose in the 200–300°C temperature range. Little information concerning the decomposition mechanism or pathway can be deduced from the single-step TG dissociation curves. Olafsson and Bryan [6] found that the first DSC curve peaks of arginine, lysine and histidine showed a relative temperature dependence at

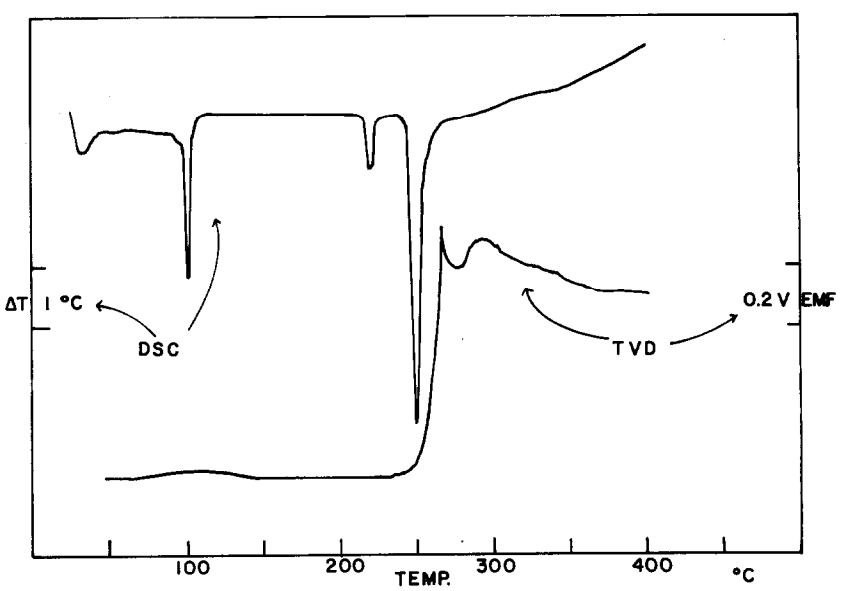

Fig. 2. DSC and TVD curves of L-arginine.

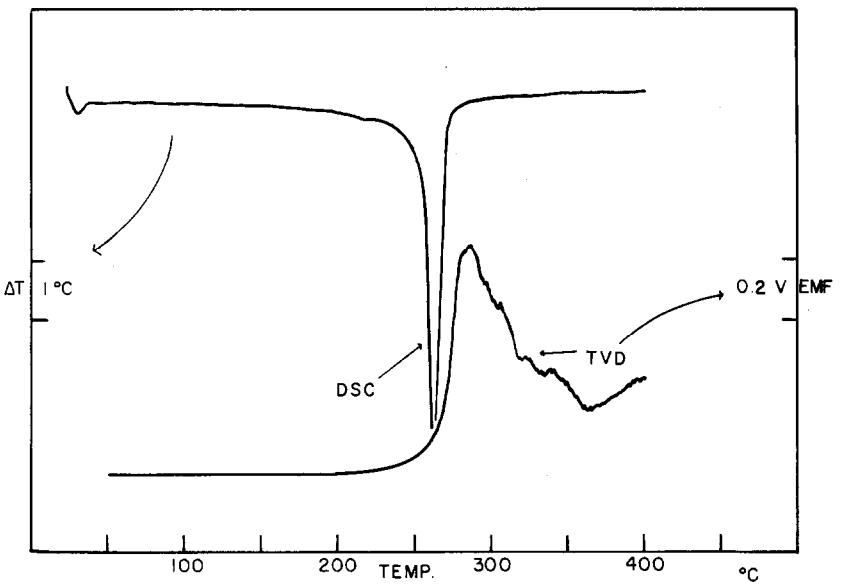

Fig. 3. DSC and TVD curves of L-glycine.

various heating rates which indicated that the origin of the peak was due to a physical rather than a chemical change. X-Ray evidence [8] indicates that L-arginine forms an unusual zwitterion in which the side-change nitrogen rather than the α-amino group is protonated and that the rings and planar groups deviate from the standard structure. The E_a for the initial decomposition step was found to be 136.9 kcal mole^{-1}, while for the first major endothermic DSC peak, E_a was 35.3 kcal mole^{-1} [6].

The TVD and DSC curves of selected amino acids are shown in Figs. 2–7.

TABLE 1

Characteristic peak temperatures for selected amino acids

Amino acid	DSC ΔT_{min}(°C)		T_{max}(°C)	
	This work	Refs. 3–6	TVD [a]	TG [b]
L-Arginine	248	246	265	285
L-Glycine	262	259	288	285
L+-Glutamine	192	196	210	228
L-Histidine	287	288	308	322
DL-Lysine·HCl	273	233 [c]	297	310
DL-Methionine	272	289	288	[d]

[a] Peak maxima temperature.
[b] Temperature for maximum slope of TG curves.
[c] For L-lysine.
[d] Not available.

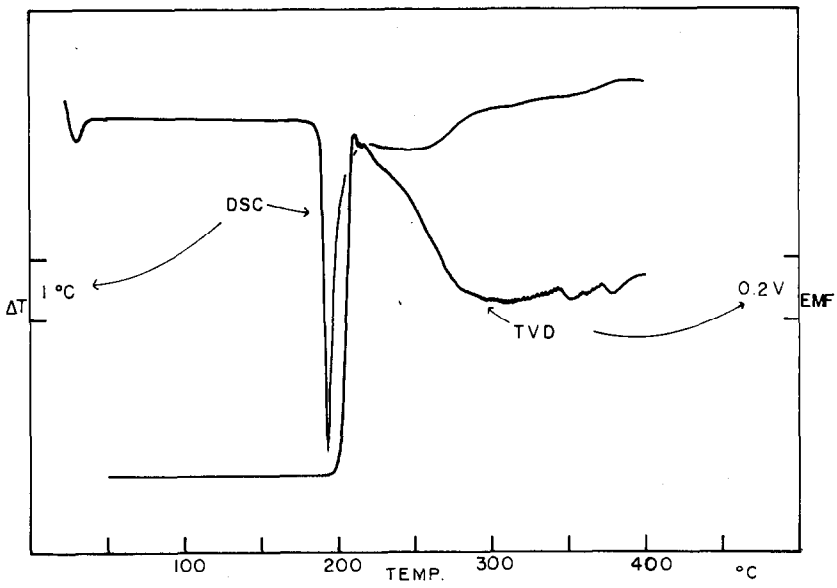

Fig. 4. DSC and TVD curves of L+-glutamine.

All of the DSC curves, with the exception of L-arginine, consist of a single curve peak with a peak minimum in the 192–314°C temperature range. These peak minima temperatures are in good agreement with those previously determined by Olafsson and Bryan [3–6]. Peak minima temperatures found in this investigation, and those of previous studies, are given in Table 1.

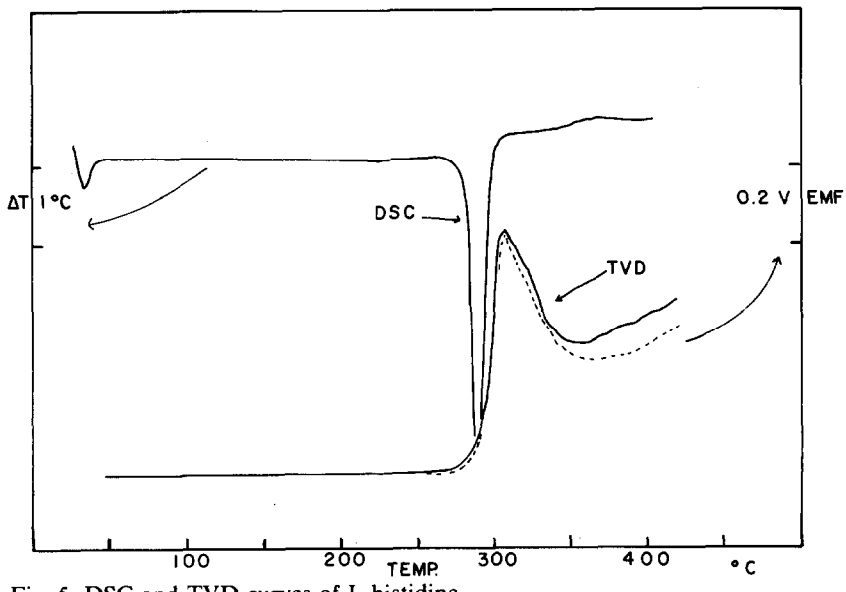

Fig. 5. DSC and TVD curves of L-histidine.

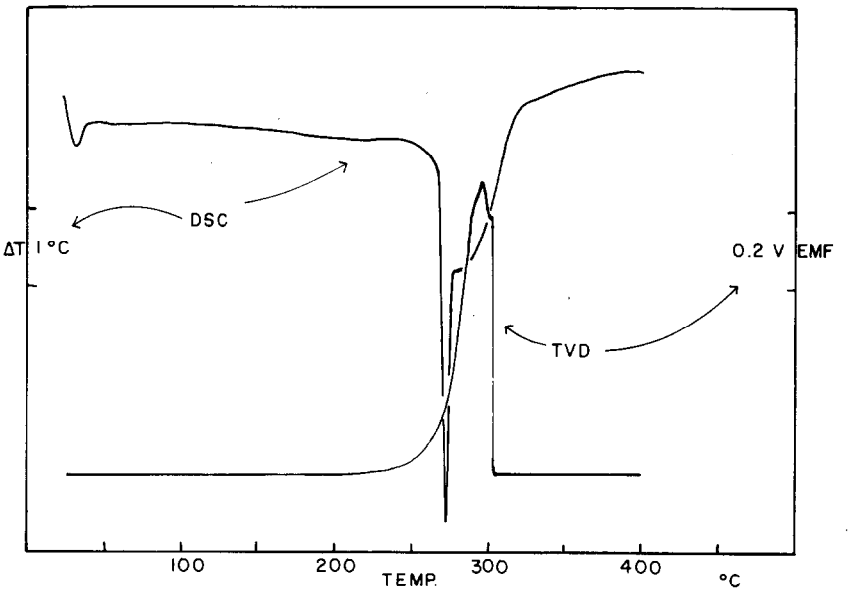

Fig. 6. DSC and TVD curves of DL-lysine·HCl.

By means of a curve resolver, Olafsson and Bryan [4] evaluated the relative complexity of the thermal decomposition reaction of selected amino acids. Of the acids described here, L-glycine contained a single component DSC curve. A double component curve was found for L + -glutamine while a triple component curve was observed for DL-methionine. While detailed intermediate reactions were not evaluated for the amino acids studied here,

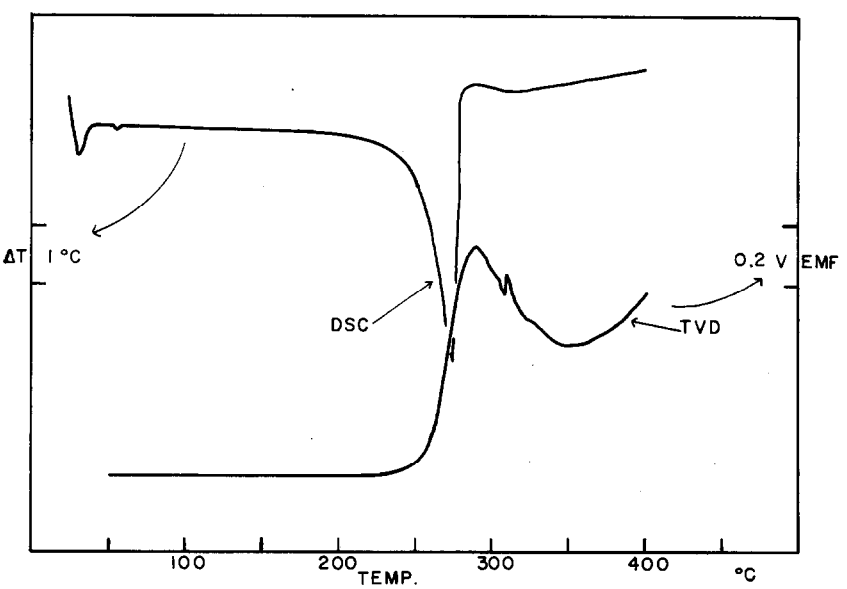

Fig. 7. DSC and TVD curves of DL-methionine.

they probably follow the same pathways of loss of ammonia and/or the evolution of carbon dioxide to yield unsaturated hydrocarbons or amines, respectively. These reactions will be discussed in a later section.

The TVD curves of the selected amino acids are shown in Figs. 2–7, along with the DSC curves.

In TVD, the EMF output, in d.c. volts, is recorded as a function of sample or system temperature. Except for L-arginine, the EMF of the TVD curves is zero volts until the decomposition reaction begins in 200–300°C temperature range. This curve reaches a maximum at a temperature in which the DSC curve peak returns to the baseline. Obviously, the kinetics of the electrode-decomposition product(s) reaction are different than those of the decomposition reaction. These electrode reactions probably involve one or more diffusion steps between the electrode surface and the amino acid or amino acid decomposition product(s), which would be different from the decomposition kinetics themselves. The leading edge of the TVD curve peaks is reproducible to within ± 1–2%, as shown with L-histidine in Fig. 5. However, after the peak maximum temperature is attained, the reproducibility falls to within $\pm 20\%$ in some cases. This is related to the electrode–amino acid decomposition products interface, which, due to the nature of the reaction, would not be expected to be reproducible. The trailing edge portion of the curve also consists of several shoulder peaks which may be related to the consecutive and/or concurrent reactions previously described in the DSC curves [5]. These reactions could produce decomposition products which would react with the aluminum metal electrode surface. An attempt is being made to elucidate the nature of these electrode reactions using ESCA and Auger spectroscopy techniques.

The primary amino acid–electrode reaction is probably similar to that previously described for succinic acid [2]. Using a general formula for an amino acid, the electrode reactions are probably

(a) aluminum electrode (−)

$$Al^0 \rightarrow Al^{3+} + 3\,e^-$$

$$3\,H_3\overset{+}{N}\text{–}\underset{\displaystyle R}{\underset{|}{C}}H\text{–}COO^- + Al^{3+} \rightarrow Al(H_2N\text{–}\underset{\displaystyle R}{\underset{|}{C}}H\text{–}COO)_3 + 3\,H^+$$

(b) platinum electrode (+)

$$3\,H^+ + 3\,e^- \rightarrow \tfrac{3}{2}\,H_2\,(g)$$

These would involve the primary electrode reactions with the amino acid; a possible secondary reaction could involve deamination reactions of the amino acid such as

$$H_3\overset{+}{N}\text{–}\underset{\displaystyle R}{\underset{|}{C}}H\text{–}COO^- \xrightarrow{-NH_3} R\text{–}\underset{\displaystyle H}{\underset{|}{\overset{+}{C}}}\text{–}COO^-$$

which might also react with the aluminum electrode via various diffusion type reactions. Decarboxylation reactions might also proceed via the aluminum electrode to give the amine, $R-CH_2-NH_2$. Also, at still higher temperature, pyrolytic reactions may take place yielding carbon or carbonacious residues.

The TVD curve peak for DL-lysine · HCl illustrates the shorting of the two electrodes by contact with each other, causing the EMF to fall to zero. No insulating mica washer was employed in this case. In the case of L-arginine, a small TVD curve peak was observed in the dehydration region of the amino acid. This peak is weak because of the small amount of water present in the amino acid molecule and also the small amount of sample. The water peak observed before the decomposition reaction was only found in L-arginine.

CONCLUSIONS

The technique of TVD yields characteristic EMF vs. temperature curves for the selected amino acids studied in this investigation. Unfortunately, the resultant TVD curves are not unique in that they yield thermal analysis information that is not inherently different from the TG and DSC data. However, the origin of the EMF output is different from that of the TG and DSC data, which is based on mass change and enthalpic change, respectively.

ACKNOWLEDGEMENT

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