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THE EMISSION THERMOPHOTOMETRY (ETP) OF SOME AMINO ACIDS

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ABSTRACT

The emission thermophotometry (ETP) curves of ten selected amino acids were determined in a flowing oxygen atmosphere. Most of the ETP curves contained a single emission peak in the 230–350°C temperature range; several of the curves contained multiple peaks and/or shoulder peaks. The light emission varied in intensity for each amino acid, but in most cases was at a very low level. The origin of the light emission process is not known but it is probably due to the presence of unstable pyrolysis products.

INTRODUCTION

The thermal properties of many of the amino acids have been studied by numerous investigators using various thermal analysis techniques. Olafsson and Bryan [1–4] used DTA, DSC and curve-resolving techniques to study the thermal dissociation, polymerization and condensation reactions of amino acids under conditions believed to have been prevalent on primordial earth. They showed that many amino acids thermally dissociate in as many as three steps, and determined the thermal stability ranges of each of these reactions as well as their kinetics (E_a).

Hung [5] used TG, DTG and gas chromatography techniques to study the kinetics of the solid-state decomposition reactions of L-serine, L-lysine, L-phenylalanine and L-cysteine. It was found that DTG provided a more rapid, sensitive, simpler and direct means for determining kinetic parameters than DTA or DSC.

Grunenberg et al. [6] used a high-sensitivity DSC technique to study the phase transition of 22 crystalline neutral aliphatic amino acids. These compounds contained nine solid-state phase transitions between 233 and 423 K. Many of the transitions were described for the first time.

Contarini and Wendlandt [7] used TG, DSC and thermovoltaic detection (TVD) to study the thermal dissociation of six selected amino acids. All of the TVD curves, except that for L-arginine, exhibited a broad EMF peak in the 200–300°C temperature range. The trailing edges of the TVD peaks

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were not very reproducible due to the irreproducible nature of the electrode–decomposition product interface. In general, the TVD curve peaks were in the same temperature range as those found in the DSC curve peaks.

In conjunction with studies on the thermal light emission of polymers, organic and inorganic compounds, coordination compounds and other substances, it was observed that many of the amino acids studied exhibited low-level emission curves when heated in an oxygen atmosphere. Although the light emission peaks in these curves appeared in the same general temperature range as those for various polymers, the light-producing mechanism must certainly be different. In order to elucidate this phenomenon in greater detail, ten amino acids were selected and studied by the emission thermophotometry (ETP) technique.

EXPERIMENTAL

ETP apparatus

The ETP apparatus used has been previously described [8]. The components used were the same as described earlier except a Schoeffel Model M460 photometer was substituted for the American Instrument Co. photometer. Circular Al cups, 6 mm diameter by 2 mm high, were used to contain the powdered amino acid samples. In most cases, a black carbonaceous residue remained in the cup after the pyrolysis reaction. A furnace heating rate of 20°C min^{-1} was employed in a dynamic oxygen gas atmosphere (flow rate, 40 ml min^{-1}).

The resulting thermal light emission curves were processed with a microcomputer data system and plotted on a dot matrix printer. In most cases, the raw data were replotted at higher photometer sensitivities than recorded, due to the low-level light emission of the samples.

Amino acid samples

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

RESULTS AND DISCUSSION

The ETP curves for the ten amino acids are illustrated in Figs. 1–5. Most of the ETP curves contained a single light emission peak in the 230–350°C temperature range (350°C was the upper temperature limit employed for these studies). Several of the curves contained multiple peaks and/or

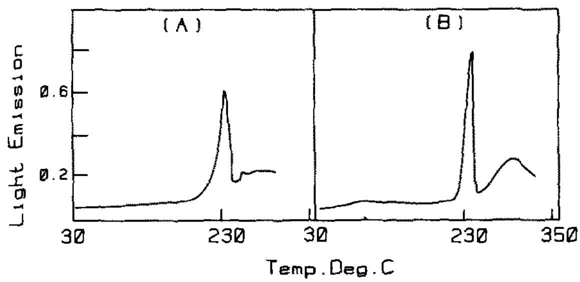


Fig. 1. ETP curves of amino acids: (A) L-phenylalanine; (B) L(+) glutamine.

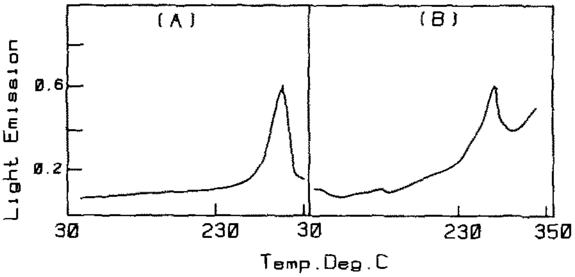


Fig. 2. ETP curves of amino acids: (A) L-valine; (B) L-glycine.

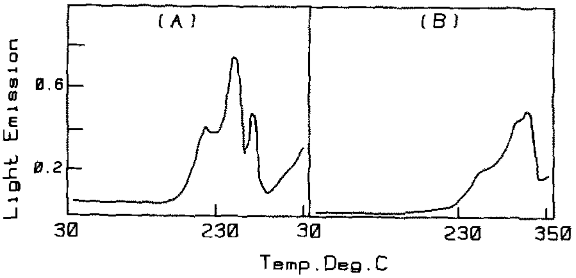


Fig. 3. ETP curves of amino acids: (A) DL-methionine; (B) DL-alanine.

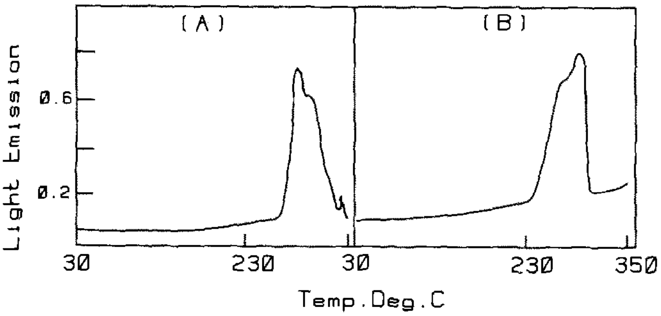


Fig. 4. ETP curves of amino acids: (A) DL-lysine·HCl; (B) L-leucine.

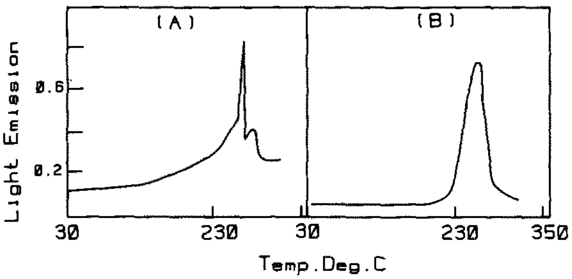


Fig. 5. ETP curves of amino acids: (A) L-tryptophan; (B) L-arginine.

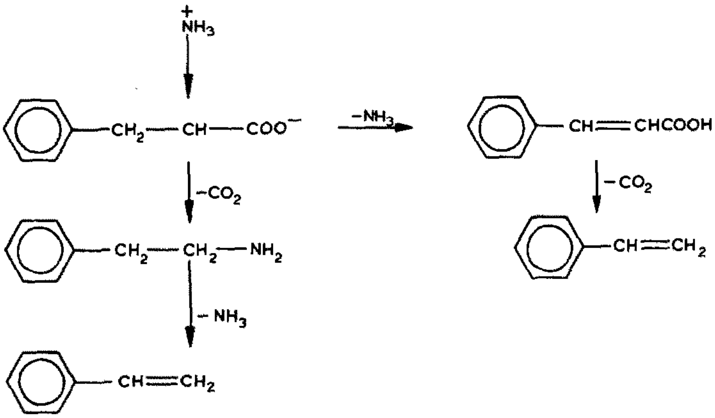
shoulder peaks on the main curve peak. The sample light emission varied in intensity, as indicated by the sensitivity factor given for each figure in Table 1. In most cases it was at a very low level, and could not be detected visually with the naked human eye. Curve peak temperature maxima are also listed for data purposes in Table 1.

Not all of the amino acids will be discussed in terms of their thermal dissociation reactions, as this has been adequately done elsewhere [1–7].

TABLE 1

ETP data for amino acids

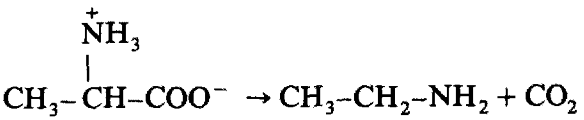
Amino acid	Peak maximum (°C)	Photometer sensitivity factor
L-Phenylalanine	230 (shoulder)	X1
L(+)-Glutamine	239 300	X2
DL-Methionine	210 250 280	X20
DL-Alanine	320 270(s)	X9
L-Tryptophan	270 280	X2
L-Arginine	263	X1
DL-Lysine·HCl	290 305	X1.5
L-Leucine	285	X1.5
L-Valine	322	X1
L-Glycine	275	X6



Scheme 1.

Phenylalanine (Fig. 1A), an aromatic amino acid, was shown [4] to exhibit a thermal decomposition curve that required a minimum of three Gaussian curves to resolve. This suggests that three steps are involved in the pyrolysis process in nitrogen. Since an oxygen atmosphere was used here, the decomposition reactions are no doubt completely different. However, the curve indicates multiple peaks suggesting at least two reactions. According to Hung [5], this amino acid dissociates (in N_2) as shown in Scheme 1. The first step of the reaction has $E_a = 210$ kJ mol^{-1}; the second stage has $E_a = 69.9$ kJ mol^{-1}; and the third stage has $E_a = 12$ kJ mol^{-1}.

A single peak was observed for glycine (Fig. 2B) and valine (Fig. 2A). This suggests a one-step decarboxylation reaction [4]:



$$\mathrm{CH_3{-}\overset{\overset{+}{N}H_3}{\overset{|}{C}}H{-}COO^- \rightarrow CH_3{-}CH_2{-}NH_2 + CO_2}$$

glycine

Shoulder peaks, either before or after the main ETP peak, were observed for alanine (Fig. 3B), leucine (Fig. 4B), lysine · HCl (Fig. 4A), glutamine (Fig. 1B) and tryptophan (Fig. 5A). Methionine (Fig. 3A) exhibited two well-defined ETP peaks as well as a shoulder peak.

The origin of light emission processes for various hydrocarbon polymers has been reviewed by Wendlandt [9], Reich and Stivala [10] and others [11]. The initiation step in the thermal decomposition of these polymers is thought to be:

$$\mathrm{PH} \xrightarrow{O_2} \mathrm{PO}_2^{\cdot}$$

or

$$\mathrm{POOH} \rightarrow \mathrm{PO}_2^{\cdot}$$

where PH = polymer; H = active hydrogen; and $PO_2^{\cdot}$ = peroxy radical. Many other reactions are eventually involved but the light emission is thought to originate during the termination step, or:

$PO_2^{\cdot} \rightarrow \text{products}^* + O_2$

$\text{products}^* \rightarrow \text{products}$

The products * may be an electronically excited ketone in which a transition of the type $n \rightarrow \pi^*$ can give rise to phosphorescence. The maximum intensity of emitted light is related to the ability of the polymer to absorb oxygen [12].

The thermal decomposition of the amino acids, which in many cases consisted of multiple reactions, may involve the formation of peroxy radicals as oxidation products. The residues examined after the pyrolysis runs were all solid, black, carbonaceous, voluminous masses. The possibility of "glowing" ignition of this residue is ruled out by the low temperature range (too low for ignition) and also the low level of the light emission. The light emission observed for the amino acids is no doubt due to the presence of certain pyrolysis products formed in an oxygen atmosphere. However, due to the limited data presented here, it is not possible to explain the exact origin of these light emission processes. The ETP curves may be used, in a limited manner, for the qualitative identification of the amino acids. Additional studies may elucidate the origin of the light emission reactions.

In general, most organic compounds, if they exist in the solid or liquid phases at these temperatures, will exhibit low-level light emission. An oxygen atmosphere must, of course, be present for this process to occur, which suggests that perhaps peroxy radicals are responsible, at least in part, for the light emission process.

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