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Communications

Formation of α-Amino Acids from β- and γ-Amino Acids by Contact Glow Discharge Electrolysis

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We have recently reported the formation of various amino acids from aliphatic carboxylic acids (*1*), aliphatic amines (*2*), and elemental carbon (*3*) by contact glow discharge electrolysis (CGDE) (*4*). In the present paper, the formation of α-amino acids by degradation of β- and γ-amino acids using CGDE is described. The CGDE was carried out in a reaction tube containing an aqueous solution (about 15 ml of water twice-distilled using a quartz distillation apparatus) of the substrate (0.001 mol). Nitrogen gas was bubbled through the solution for 2 hr before applying the CGDE and also during the course of the reaction. The applied electric current was 50–60 mA at 500–1500 V. The reaction temperature was kept at 20–30°C by cooling the reaction tube in a methanol–dry ice bath. After the reaction was over, the solution was diluted appropriately for amino acid analysis (amino acid analyzer: Yanagimoto Model LC-5S). The reaction mixture was also treated with dinitrofluorobenzene, and the resulting dinitrophenyl(DNP)-amino acids were separated by thin-layer chromatography. The major products were identified by comparing the R_f values with those of authentic DNP-amino acids.

The results of the degradation reaction of β- and γ-amino acids and of few α-amino acids are summarized in Table 1. The β-amino acids such as β-alanine (β-Ala) and β-aminobutyric acid (β-ABA) give rise to glycine (Gly) and alanine (Ala), respectively, by the degradation reaction using CGDE. In the case of γ-ABA, Gly and β-Ala are obtained as stepwise degradation products (Fig. 1). The yield of Gly (24 or 17% from β-Ala or γ-ABA, respectively) is considerably higher than those observed in earlier amino acid syntheses by CGDE (*1*, *2*). Very few other ninhydrin-positive materials were found in the reaction mixture.

In order to examine the mechanism of the degradation, the CGDE of α-methyl-β-alanine(α-methyl-β-Ala) was carried out. The main product of the degradation is not Ala (0.7%) but Gly (14%). The Gly is obtained by degradation of the methylene group bound to the carboxyl. Therefore, from the results obtained above, it can be assumed that the α-methylene group bound to the carboxyl group of γ-ABA is eliminated stepwise by CGDE as follows:

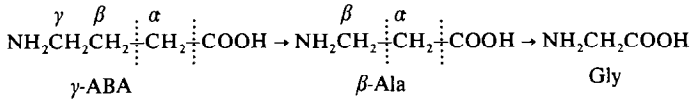

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TABLE 1

DEGRADATION AND/OR CONVERSION OF AMINO ACIDS BY CGDE[a]

Substrate (0.001 mol)	Reaction time (min)	Products (percentage yield)	Recovery of substrate (%)
β-Ala	15	Gly(8.4) } one unknown peak	76
	60	Gly(24) } one unknown peak	18
	120	Gly(14) } one unknown peak	3
β-ABA	60	Ala(4.7), Asp(1.3), Gly(0.7), Ser(0.6), two unknown peaks	—[b]
α-Methyl-β-Ala	60	Gly(14), Ala(0.7), β-Ala(0.7), α-ABA(0.3), four unknown peaks	14
γ-ABA	25	Gly(7.1), β-Ala(8.5) } four unknown peaks	36
	60	Gly(17), β-Ala(7.1) } four unknown peaks	4.8
	120	Gly(15), β-Ala(2.8) } four unknown peaks	0.2
Glu	60	Asp(7.7), Gly(3.5), four unknown peaks	9.9
Ala	60	Ser(0.5), Gly(0.5), four unknown peaks	3.4
α-ABA	60	Asp(6.0), Gly(2.3), Thr(1.3), Ala(0.1), Ser(0.09), five unknown peaks	3.1

[a] Ala, alanine; ABA, aminobutyric acid; Ser, serine; Gly, glycine; Asp, aspartic acid; Thr, threonine; Glu, glutamic acid.

[b] Ninhydrin negative.

This scheme was also supported by the fact that glutamic acid (Glu) gives aspartic acid (Asp) as a main product by CGDE. On the other hand, α-amino acids such as Ala and α-ABA are converted into other amino acids, e.g., serine, Gly, Asp, etc.

The formation of α-amino acids from β- or γ-amino acids is interesting both as an organic reaction and as a prebiotic source of α-amino acids. In an evolutionary context, this finding suggests that α-amino acids could also have been formed by CGDE from β- and γ-amino acids which were synthesized by electric discharge (*1*, *2*, *5–7*). CGDE can be regarded as a simulation of lightning striking on the primitive sea.

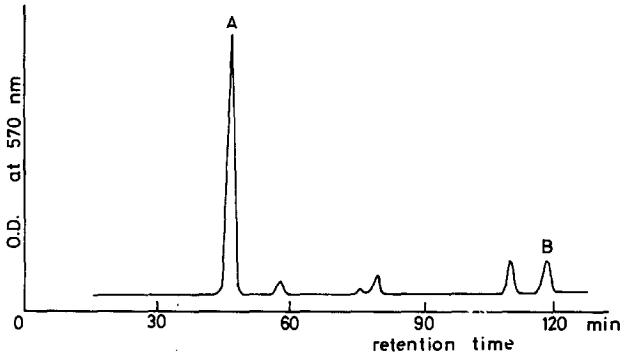

FIG. 1. Formation of amino acids from γ-ABA by CGDE for 1 hr. A, Gly (17%); B, β-Ala (7.1%); other peaks are of unknown amino acids.

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