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SYNTHESES OF AMINO ACIDS FROM ALIPHATIC AMINES BY CONTACT GLOW DISCHARGE ELECTROLYSIS*

Kaoru HARADA** and Tameo IWASAKI***
Institute for Molecular and Cellular Evolution
Department of Chemistry, University of Miami
Coral Gables, Florida 33134

Amino acids are synthesized from aliphatic amines by direct carboxylation using formic acid under conditions of contact glow discharge electrolysis.

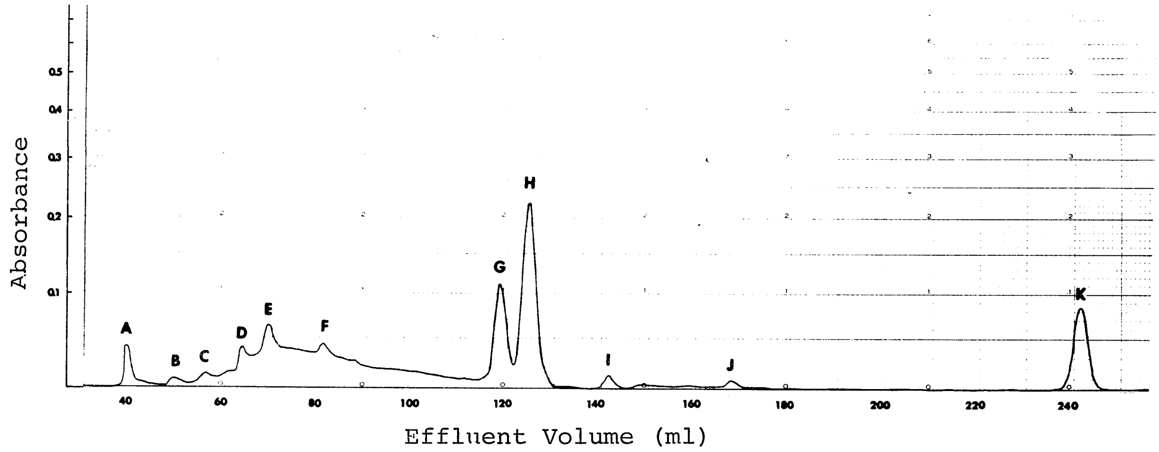
Glow discharge electrolysis (GDE) has been applied mainly to the study of inorganic compounds such as water, ammonia or metal ions in aqueous solutions.[1,2] However, the chemistry of organic compounds subjected to GDE has received little attention.[3-7]

The present paper reports the formation of amino acids by contact glow discharge electrolysis (CGDE) from several aliphatic amines (or amino acids) by direct carboxylation using formic acid (or formamide)in aqueous solution.

Two types of electrolysis tubes were used for CGDE. One is a U-shaped tube (U), the other a single straight tube (S). In the U-tube, the cathode and anode compartments were separated by a fine porosity glass frit; CGDE was carried out in the anodic compartment. The carboxylation reactions of amines (0.0025 mol) were carried out in aqueous formic acid solution (30%, 10 ml) at 10-25°C for 1-3 hrs. The applied electricity (DC) was 450-600 V and 20-100 mA. After the reactions were over, the reaction mixtures were evaporated to dryness under reduced pressure and the residues were diluted appropriately for amino acid analyses. The reaction products were also treated with 2,4-dinitrofluorobenzene and the resulting DNP-amino acids were separated both by column and thin layer chromatographies. The major amino acid products were confirmed as DNP-amino acids.

Fragmentation of amino acids (or their precursors) during CGDE was observed. It seems there are some regularities in the fragmentation. These are: a) decarboxylation of carboxylic acid, b) cleavage of α-β linkage and c) possible hydroxylation of amino acids. The amino acid products were rather clean in composition and most of the major products could be explained by carboxylation reaction and the fragmentation mentioned above.

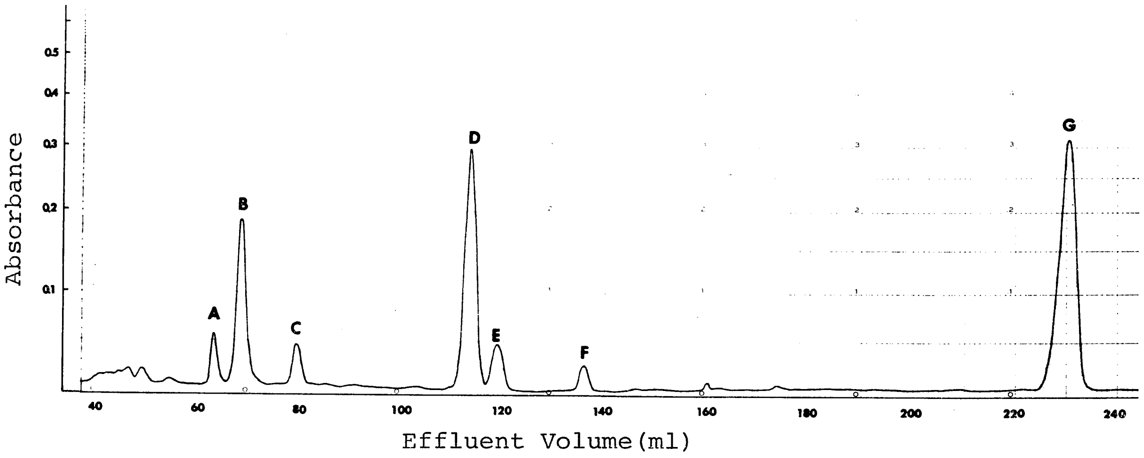
The yield of amino acids in some carboxylation reactions reached 9%. However, these amino acid formations by CGDE do not represent the optimum conditions. The CGDE is characterized by rather low voltage of electric discharge and by a relatively high does rate. The approximate expenditure of energy for the formation of carboxylation reactions is 0.1 to 0.3 kcal per 10^{-6} mol of amino acid(s).



Reaction 2 $CH_2CH_2NH_2 \xrightarrow[CGDE]{HCOOH}$ glycine, alanine, β-alanine, aspartic acid

A,B,C,D, unknown; E, aspartic acid; F, unknown;

G, glycine; H, alanine; I,J, unknown; K, β-alanine



Reaction 5 $H_2N\text{-}CH_2CH_2\text{-}COOH \xrightarrow[CGDE]{HCONH_2} \xrightarrow[H^+]{H_2O}$ aspartic acid, glycine, alanine, β-alanine

A, unknown; B, aspartic acid; C, serine(?); D, glycine, e, alanine; F, unknown; G, β-alanine

Fig. 1. Carboxylation of ethylamine and β-alanine by CGDE

TABLE I

Direct Carboxylation of Amines (Amino acids) by Contact Glow Discharge Electrolysis(CGDE)

	Starting material (mol)	Reaction tube	HCOOH 30%, ml (mol)	Temp (°C)	Time (hr)	Voltage V	Current mA	Amino acids found in the reaction product (Yield) a)
1	CH_3NH_2 (0.0025)	S	10	-10~+5	2	500-510	50	glycine (12%) and 6 unknown peaks
2	$CH_3CH_2NH_2$ (0.0025)	S	10	10	2	460-520	50-60	glycine (1.3%), alanine (2.6%), β-alanine (4.3%) and 8 unknown peaks
3	Pyrrolidine (0.0025)	S	10	10	1	500-510	65-70	proline (3.5%), isoproline(?) (4.98%), glycine and 7 unknown peaks
4	alanine (0.0025)	U	10	15	2	530-550	60	aspartic acid (1.2%), glycine (3.2%), alanine (13.6% was recovered) and 4 unknown peaks
5	β-alanine (0.0025)	U	$HCONH_2$ (0.005) NaOH (0.0025) H_2O 10	38	0.75	500	75	aspartic acid (1.6%), glycine (2.6%), alanine (0.5%), β-alanine (14.7% was recovered) and 5 unknown peaks
6	α-amino-butyric acid (0.0025)	U	10	15	2	530-550	60	glutamic acid (5.9%), glycine (2.1%), alanine (0.2%), α-aminobutyric acid (8.7% was recovered) and 12 unknown peaks

a) The yields were determined by an automatic amino acid analyzer.

However, for the prolonged reaction, the energy is increased to 1 Kcal. The expenditure of energy in the CGDE is much lower than that used in various other types of prebiotic formations of amino acid(s) (2-220 kcal/10^{-6} mol of glycine)[8].

Application of GDE to organic compounds is a new area of chemistry. GDE is also interesting as a possible method for the synthesis of bioorganic compounds under prebiotic conditions.

The representative results are summarized in Table I and are also shown in Fig. 1.

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** Present address: Department of Chemistry, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaragi-ken, 300-31.

*** Present address: Department of Synthetic Chemistry, Research Laboratory of Applied Biochemistry, Tanabe Seiyaku Co., Ltd., 16-89, Kashima-3-chome, Yodogawa-ku, Osaka 532.

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