Studies on the Synthesis of Protein Analogus (Part II)
Heat Decomposition of N-carbothiophenyl-amino acids*

By

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In the first report[1] it was remarked that N–carbothiophenylamino acids expelled thiophenol and carbon dioxide and were polymerized in polypeptides and this main reaction formed polypeptides, but at the same time the subreactions called "branched type "or" ringtype" occured. The thermolysis curves showed that each amino acid had the same tendency of decomposing, but the temperatures of the decomposition differed a little according to the kind of amino acids. So, in order to investigate the conditions of thermolysis further, we observed the thermolysis curves at the constant temperatures of 130 ℃, 140 ℃ and 150 ℃, and obtained the activation energy in the main reactions. The samples used are as follows : carbothiophenyl–DL–alanyl-glycine, carbothiophenyl– ε–aminocaproic acid, carbothiophenyl–L–glutamic acid ,carbothiophenyl–L–glutamic acid anhydride, carbothiophenyl–L–leucine, carbothiophenyl–DL–α–aminolauric acid, carbo– thiophenyl–DL–alanine, carbothiophenyl–β–alanine, carbothiophenyl–DL–phenylalanine and carbothiophenyl-glycine. All of them were prepared by the method discussed in the previous report.[1]

Taking up about 20 mg. of each sample, we observed the relative curve between the residual sample and the reaction time with thermobalance. The results are shown in Fig. 1.

Though no curves completely show linear reactions, the main parts are nearly straight, from which we get the reaction velocity constant K. The relations between log K and 1/T, which are the straight lines, are shown in Fig. 2.

The activation energies which are calculated from them are shown in Table 1.

In the block polymerisations, it is much easier to polymerize glycine, DL–alanine, β–alanine, ε–aminocaproic acid, L–leucine and DL–phenylalanine, in which the reactions seem to complete at about 150—160 ℃,[2] than to polymerise DL–α–aminolauric acid, DL–alanylglycine, L–glutamic acid and L–glutamic acid anhydride, in which the complete decompositions do not occur unless in a higher temperature. In such high temperature, it is very difficult to obtain the polypeptides having high molecular weights, for the subreactions will occur extensively. There seems to be no interrelation between these activation energies and the polymerisabilities of amino acids.

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1) Jan. of the Chem. Soc. of Japan 74, 961 (1953)
2) J. Noguchi, Jan. of the Chem. Soc. of Japan 74, 962 (1953) Fig. 2.

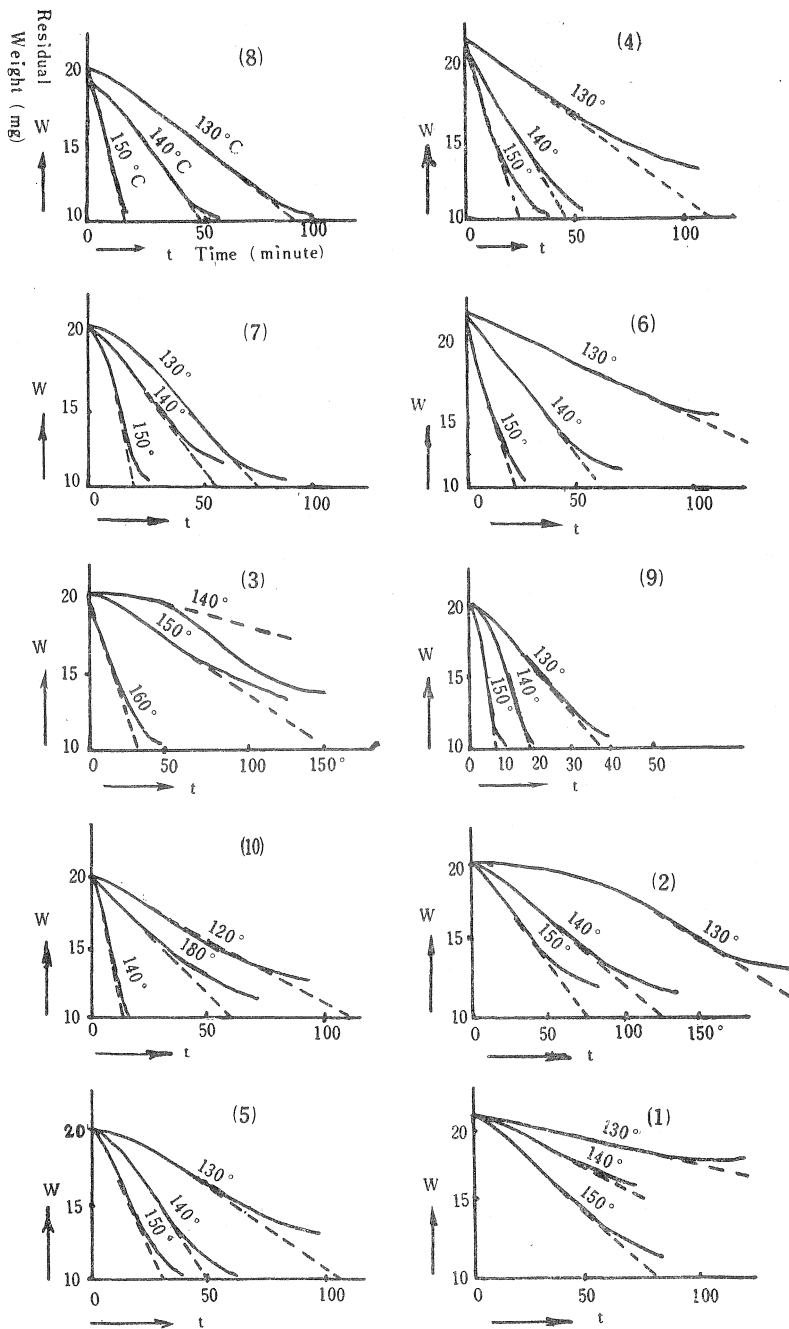Fig. 1 Thermolysis of N–carbothiophenyl–amino acid at 130°, 140°, 150℃.

（1） Cps–glycine,
（3） Cps–glutamic acid anhydride,
（5） Cps–glutamic acid,
（7） Cps–ε–aminocaproic acid,
（9） Cps–β–alanine,

（2） Cps–DL–phenylalanine,
（4） Cps–α–aminolauric acid,
（6） Cps–DL–alanine,
（8） Cps–alanylglycine,
（10） Cps–L–leucine
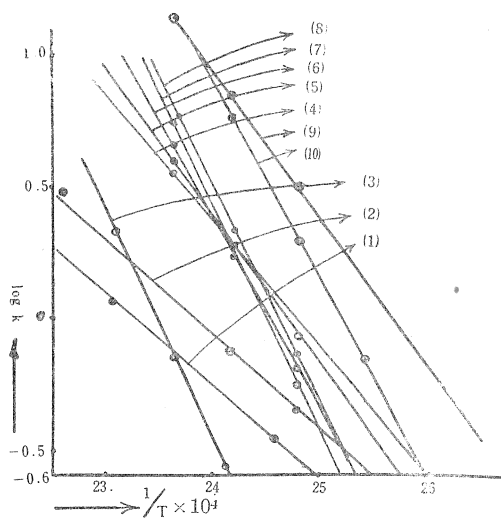
Fig. 2

Table　1

Carbothiophenyl–amino acid	activation energy (Kcal)
Glycine	16.13
DL–phenylalanine	16.58
DL–α–aminolauric acid	21.64
β–alanine	25.54
L–glutamic acid	25.68
DL–alanine	33.13
L–leucine	33.98
DL–alanyl–glycine	37.03
ε–aminocaproic acid	38.75
L–glutamic acid anhydride	40.66