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Studies of the Rates of Thermal Decomposition of Glycine, Alanine, and Serine

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Abstract—Rates of thermal decomposition of glycine, alanine, and serine are described by the equation of first order reaction in the temperature range 200–300ºC. Apparent rate constants and apparent activation energies of decomposition of α-amino acids were evaluated. It was found that the main gaseos reaction product is carbon dioxide.

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Glycine, alanine, and serine participate in various metabolic processes taking place in living organism. Glycine exhibits the retarding action upon the nervous system and also neutralizes the ill effect of benzoic acid. It is widely used in manufacturing of fertilizers [1], explosive mixtures [2], and in the food industry [3]. Alanine is used for preparing carnosine, the anticataractive ophthalmologic remedy. It is also used in manufacturing of fertilizers [1, 4]. Serine takes part in formation of the monocarbon enzyme [5].

During the thermal treatment of the protein-containing food stuffs the amino acids formed in the course of hydrolysis are exposed to the action of temperature. The aim of this work is the investigation of thermal decomposition of the amino acids (glycine, alanine, and serine), and establishing of the composition of products formed in the course of thermal degradation of compounds under study.

For establishing the temperature corresponding to the beginning of thermal decomposition of amino acid the sample under investigation was placed in the reactor which was evacuated to the residual pressure 2×10^{-2} Torr. The sample was heated slowly at a rate 4ºC/min.It turned out that noticeable decomposition of the amino acids accompanied by formation of the volatile products was observed at the temperatures considerably lower than their melting points. For instance, gaseous products were formed at 210ºC while heating of glycine (mp 262ºC), at 240ºC for alanine (mp 297ºC), and at 200ºC for serine (mp 228ºC). Results presented in Fig. 1 permitted to choose the optimal temperature range for the measurements of rates of decomposition of the amino acids.

Decomposition of glycine proceeded with the clearly expressed induction period (Fig. 2). The time of heating the reagents to the given temperature was 8–15 min (average), and the pressure of gases corresponding to the given temperature was accepted as the initial pressure p_0. The character of curves reflecting the alteration in pressure with the time of heating shows that decomposition of the crystalline glycine corresponds to the class of topochemical reactions. Inductive period corresponds to the growth of active centers (nuclei). Time of the inductive period at 212ºC is 30 min.

Joining of separate nuclei leads to the formation of the common reaction front. Under the conditions of the stationary reaction front linear dependence of pressure on time is observed. After that the rate of liberation of the volatile product sharply decreases and stops after the completion of the process (Fig. 2).

The character of variation in the pressure of the volatile products of decomposition of glycine presented in the pressure (p)–time (t) coordinates permits to establish the range of the intense gas liberation (middle part on the curves excluding the induction period of decomposition), and on its basis to evaluate the apparent rate constants. In this case the calculation of rate constants of the general process may

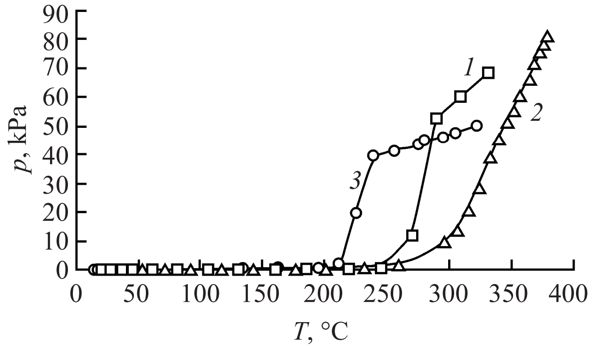


Fig. 1. Dependence of pressure of the decomposition products on temperature; (*1*) glycine, (*2*) alanine, and (*3*) serine.

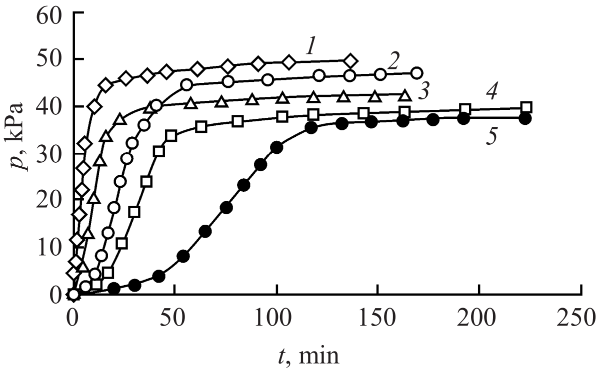


Fig. 2. Dependence of pressure (*p*) on time (*t*) for glycine, ºC: (*1*) 239.5 , (*2*) 231 , (*3*) 226, (*4*) 220, and (*5*) 212.

be formally carried out according to the first order equation.

$$k = (1/t)\ln[(p_\infty - p_0)/(p_\infty - p_t)].$$

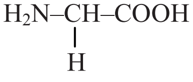
Here p_0 and p_∞ are the initial and the final gas pressure in the range of measurement of the intense gas evolution; p_t is the gas pressure at the time t.

Rate of the overall process is regarded as the assembly of all parallel and consecutive elementary reaction on the solid-gas border as well as in the gas phase.

No induction period is observed for alanine (Fig. 3).

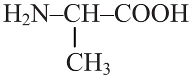
Alanine sublimes easily, and depending on temperature of the experiment the initial pressure p_0 varies from 18 to 157 mm. Methyl group of alanine increases thermal stability of this compound as compared to glycine. Similarly to glycine, the apparent rate constants of the process of decomposition of alanine were calculated according to the equation of the first order reaction.

In the series of the amino acids under investigation serine contains the additional hydroxymethyl group.



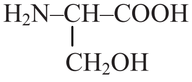
$H_2N\text{–}\underset{\displaystyle H}{CH}\text{–}COOH$

glycine



$H_2N\text{–}\underset{\displaystyle CH_3}{CH}\text{–}COOH$

alanine



$H_2N\text{–}\underset{\displaystyle CH_2OH}{CH}\text{–}COOH$

serine

Just this circumstance leads to the sharp decrease in thermal stability of serine as compared to glycine and alanine. The character of variations in pressure of the gaseous reaction products on time is presented in the Fig. 4. The plot in the pressure (*p*)–time (*t*) coordinates has two clear parts. The first part corresponds evidently to decomposition of the amino acid while the second one reflects the increase in pressure caused by decomposition of the reaction products. We used the first plot for the calculation of the apparent rate constants of the first order reaction.

Dependence of rate constants of thermal decomposition of the amino acids in the ln k–$1/T$ coordinates

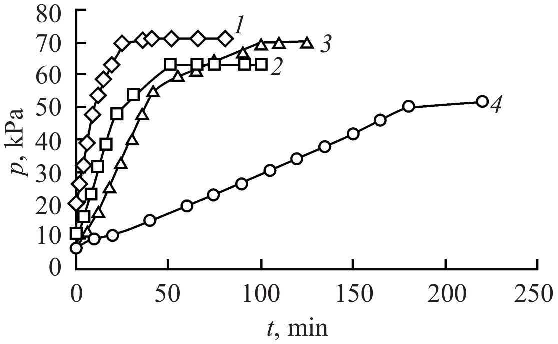


Fig. 3. Dependence of pressure (*p*) on time (*t*) for alanine, ºC: (*1*) 309 , (*2*) 277, (*3*) 264, and (*4*) 241.

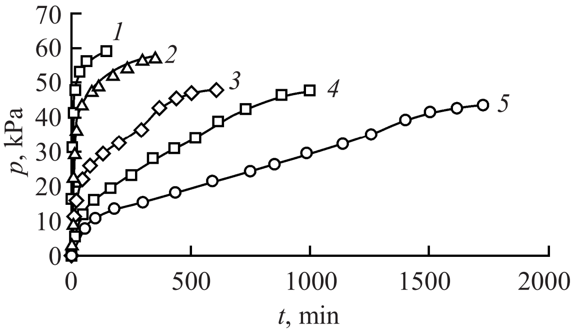


Fig. 4. Dependence of pressure (*p*) on time (*t*) for serine, ºC: (*1*) 222, (*2*) 216, (*3*) 208, (*4*) 203, and (*5*) 198.

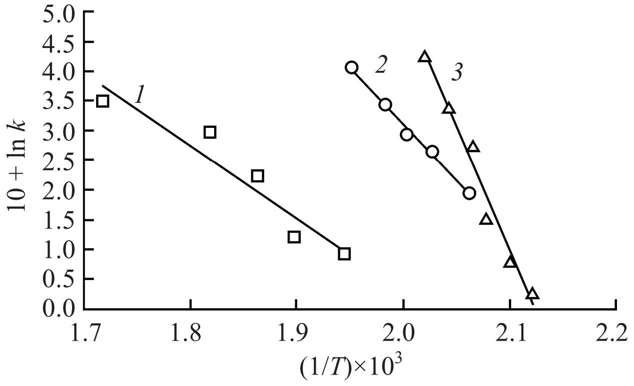


Fig. 5. Temperature dependences of the apparent rate constants: (*1*) alanine, (*2*) glycine, and (*3*) serine.

is presented in Fig. 5. In these coordinates the points of corresponding amino acid lie satisfactory on the straight lines of the Arrhenius dependences. Values of the apparent activation energies and the logarithms of the preexponential factors of the Arrhenius equations are listed below.

Amino acid	Glycine	Alanine	Serine
Temperature range of decomposition , T, °C	212–240	241–309	198–222
E_A, kJ mol^{-1}	157±7	101±19	344±29
Ln k_0	30.80	14.73	77.84
mp of the amino acid [6]	262	297	228

Analysis of the gas phase obtained after decomposition of glycine showed that the main reaction products are CO_2 and water. Small amounts of ammonia and methylamine were also found. In the case of alanine together with carbon dioxide ammonia is present. Decomposition of serine yields only carbon dioxide. Analysis of liquid phase obtained after decomposition of glycine at 220ºC showed the presence of acetic acid, of formamide, acetamide, and *N*-methylacetamide, of *n*-butyramide and propionamide. It may be concluded that prolonged heating of glycine, alanine, and serine at the temperatures about 200ºC that is 30–50ºC below their melting points causes their decomposition with the formation of volatile and liquid substances. Some of them, amides, are probably cancerogenic for humans.

EXPERIMENTAL

Crystalline glycine and l-serine of "pure" grade and *L*-alanine of "chemically pure" grade were used.

Studies of rate of decomposition of the amino acids were carried out in a thermostate using the evacuated 30 cm^3 glass ampules having thin membrane. About 20 mg samples of substances under investigation were used, and the reaction rate was monitored by the increase in the pressure of the volatile decomposition products at the given temperature of experiment. Increase in the pressure was measured by means of compensational method maintaining the zero position of membrane by means of the outer pressure. Scheme of the installation is described in [7]. Analysis of liquid phase after decomposition of the amino acids was carried out on the FOCUS DSO chromatomass spectrometer using the TR5 capillary column (60000×0.25 mm). Samples of the liquid under study, 0.05 mcl, were loaded in the injector of the chromatograph heated to 250ºC . Carrier gas (helium M 60 grade) flow rate was 1 ml min^{-1}. Temperature of column varied from 50 to 250ºC . Mass spectra were measured in the range 29–500 atomic units. Identification of the mixture components was carried out using the NIST 2003 electronic library of mass spectra. Analysis of gas phase was carried out on a MI1202 mass spectrometer at the temperature of source and the admission system 25ºC. Energy of the ionizing electrons 70 eV. Identification of components was carried out by comparison of the data obtained with the mass spectra of the NIST electronic library.

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