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Kinetics of Thermal Decomposition of Sulfur-Containing Amino Acids

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Abstract—Rates of thermal decomposition of sulfur-containing amino acids such as *D,L*-methionine, *L*-cysteine, and *L*-cystine are studied. It is established that the amino acids decompose at 190–240°C to give the gaseous and liquid decomposition products in the polyphasic system formed. The rate of summary process is described by the first order kinetic equation up to 30–50% conversion. In spite of close values of the effective activation energies of thermal decomposition of *D,L*-methionine, *L*-cysteine, and *L*-cystine (195, 193, and 184 kJ mol^{-1} respectively) the effective rate constants at one and the the same temperature differ by one or two orders of magnitude in the above-mentioned series. Sulfur-containing compounds prevail in the gaseous decomposition products, while in the liquid phase the nitrogen-containing ones are accumulated.

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Amino acids are constantly used by organisms for the synthesis of proteins and some other substances such as hormones, amines, alkaloids, coferments, and pigments. Excess amino acids under mild conditions are decomposed to the final products (in the human and mammalian organisms CO_2, H_2O, and urea are formed) with the liberation of energy necessary for the organism [1].

L-Methionine, $CH_3SCH_2CH_2CH_2CH(NH_2)COOH$, (*L*-Met) is an irreplaceable sulfur-containing amino acid (the daily need of a man is 2.5–3 g) which plays the role of a methyl group donor in organism. It is one of the precursors of choline, adrenaline, and some other biologically active compounds, and plays the role of the sulfur source in the biosynthesis of cysteine. Deficiency of *L*-Met in the food of animals and man causes the disorder in biosynthesis of proteins, the deceleration of growth and development of organism, and to the serious functional disturbances. For the enrichment of animal forage and human foodstuff as well as the medicinal remedy is used *L*-Met prepared from 3-methylthiopropanoic aldehyde and also isolated from the casein hydrolizate [1] is used.

L-Cysteine $HSCH_2CH(NH_2)COOH$ (*L*-Cys) is the substitutable sulfur-containing amino acid synthesized in organism from *L*-Met and serine with the participation of ATP. Due to high reactivity of the SH group it plays an important role in metabolism. It acts also as a protector of organism binding the heavy metals (by mercaptide formation), the arsenic compounds, the cyanides (by thiazolidine formation), and the aromatic hydrocarbons (by forming the mercapturic acids). *L*-Cys is used also as radioprotective remedy, and also as the medicinal preparation on the early stages of development of the eye cataract [1].

L-Cystine $[HOOCCH(NH_2)CH_2S]_2$ (*L*-Cys_2) is contained in the hair and wool keratin. The covalent disulfide bridges forned by the *L*-Cys_2 residues between the polypeptide chains and inside of them form the of proteins and biologically active peptides. Preservation of the disulfide bonds provides the properties of keratin and also the normal activity of hormones and ferments. *L*-Cys_2 is the replaceable amino acid. Its biosynthesis and metabolism are tightly connected with *L*-Cys, and mutual transformation of these amino acids easily takes place in living organisms [1].

Amino acids appear in organism due to the cleavage (hydrolysis) of proteins. The protein-containing foodstuff as a rule is exposed to thermal treatment. That is why it is important to know how the duration of such treatment affects the amino acids

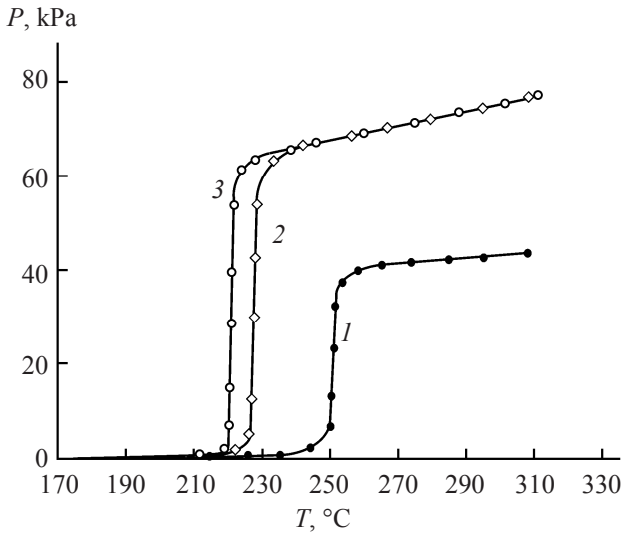

Fig. 1. Dependence of pressure of the gaseous decomposition products of (*1*) *D,L*-Met, (*2*) *L*-Cys_2, and (*3*) *L*-Cys on temperature.

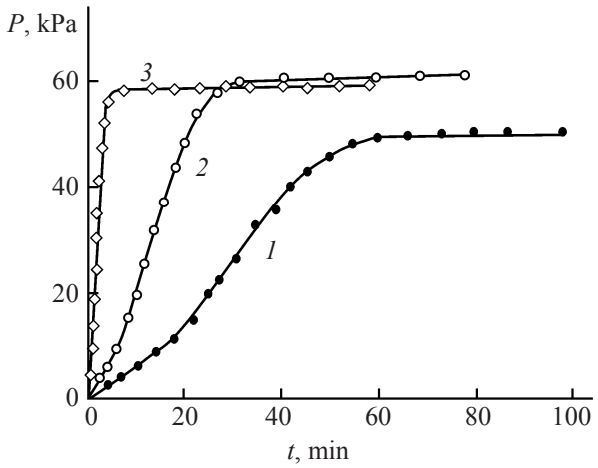

Fig. 2. Dependence of pressure of the gaseous products of decomposition of (*1*) *D,L*-Met (226°C), (*2*) *L*-Cys (224°C), and (*3*) *L*-Cys_2 (225°C) on time.

formed by the cleavage of proteins, what decomposition products are formed, and to what extent these substances are harmful for living organisms.

The aim of this investigation is the evaluation of kinetic parameters of thermal decomposition of sulfur-containing amino acids: *D,L*-Met, *L*-Cys, and *L*-Cys_2 and study of the composition of substances formed in the course of thermolysis of starting compounds. Practically no data concerning this problem is reported about [2, 3]. The workers [4] have evaluated the activation energy of decomposition of crystalline methionine in presence of air oxygen.

The rate of the summary process was monitored by the alteration of pressure of the volatile products formed at the thermolysis of amino acids in the glass reactor of constant volume. According to the DTA data obtained by us and that reported by the workers [5] *D,L*-Met is melted with decomposition at 28°C, *L*-Cys_2 at 260°C, and *L*-Cys at 240°C. When the samples are heated at a rate 3°C per minute in the closed evacuated vessel, gas evolution indicating thermal decomposition of the amino acids begins at 190–200°C. The character of alteration in pressure of the volatile components at the increase of temperature is presented in Fig. 1.

For *L*-Cys and *L*-Cys_2 intense increase in pressure of the volatile components is observed in the temperature range 220–230°C, and for *D,L*-Met at 250°C. The irreversible increase in pressure shows that thermal decomposition of the reaction mixture takes place. At the temperatures above the range of intense decomposition of the amino acids linear dependence of the increase in pressure on temperature is observed. It shows that the reaction has finished. Increase in pressure proceeds due to heating of the gaseous products of decomposition of the amino acids accoding to the equation of the ideal gas condition.

The character of dependence of pressure on temperature permitted to establish the temperature ranges convenient for the quantitative measurement of the rate of the amino acid decomposition by measuring alteration in pressure of the volatile products on the reaction time t at a constant temperature. The rate of decomposition of *D,L*-Met was studied in the temperature range 210–240°C, and of *L*-Cys and *L*-Cys_2 at 190–230°C.

In Fig. 2 kinetic curves of decomposition of sulfur-containing amino acids in the pressure (p)–reaction time (t) coodinates are presented. Thermal decomposition of amino acids submits to the equation of the first order reaction up to 30–50% conversion. The effective first order rate constants were calculated according to the following equation:

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

Here k is the reaction rate constant; p_0 is the pressure of gas over the reaction mixture in the moment of beginning of chemical transformation ($t = 0$); p_∞ is the

Table 1. Kinetic and activation parameters of decomposition of sulfur-containing amino acids

Amino acids	T, °C	$k\times0^5$, s^{-1}	$k_{220}\times10^5$, s^{-1}	E, kJ mol^{-1}	Log k_0
D,L-Met	216	5.8±0.2	8.7±0.5	195±10	16.6±0.6
	221	11.1±0.3			
	226	12.0±0.3			
	231	28.0±0.4			
	236	36.0±0.5			
Cys	194	42±7	1000±11	193±15	18.5±0.9
	198	88±11			
	201	141±14			
	206	316±60			
	225	1213±90			
Cys_2	199	21±2	143±15	184±7	16.6±0.2
	204	28±2			
	210	45±3			
	218	124±11			
	224	195±15			

Table 2. Results of mass spectral analysis of the gaseous products of thermal decomposition of sulfur-containing amino acids at 240°C.

Product	*D,L*-Met Yield, mol %	*L*-Cys Yield, mol %	*L*-Cys_2 Yield, mol %
H_2S	1.2	98.91	97.93
CO_2	55.3	0.18	0.32
NH_3+CH_4	0.4	–	–
N_2	1.0	–	0.05
CH_3SH	41.9	–	–
$(CH_3)_2S$	0.02	–	–
$(CH_3)_2S_2$	0.1	–	–
C_2H_5SH	–	0.09	0.52
C_3H_7SH	–	–	0.1
CH_3CN	–	–	0.31
C_4H_4S (thiophene)	–	0.32	0.31
C_6H_8N (methylpyridine)	–	–	0.12
C_4H_5NS (metylthiazole)	–	–	0.03
C_4H_9NS (methylthiazolidine)	–	0.14	–

largest gas pressure achieved after the completion of the overall reaction; p_t is the current gas pressure (t differs from 0). Temperature dependence of the reaction rate constants submits to the Arrhenius equation $k = k_0\exp[-E/(RT)]$. Kinetic and activation parameters of decomposition of the amino acids are presented in Table 1. The rate of decomposition of the amino acids increases in the series Met < Cys_2 < Cys, and the apparent activation energies of thermodecomposition (E) are close to one another and fall within the range 184–195 kJ mol^{-1}.

Thermal decomposition of sulfur-containing amino acids includes a set of parallel and consecutive radical reactions. At first the reaction centers appear on the surface of crystals. They look like the dark brown dots, and at this time the gaseous products appear. In the further stages of decomposition formation of the liquid phase takes place. In fact from the very beginning of decomposition of crystals the polyphasic system is formed. Not only the amino acid, but also the intermediate compounds unstable under the conditions of experiment act as the source of the volatile products. The composition of volatile products evaluated from the mass spectral data is listed in Table 2.

The main gaseous products of decomposition of *D,L*-Met are (mol%) CO_2 (55.8) and CH_3SH (41.9). Decomposition of *L*-Cys and *L*-Cys_2 is accompanied by evolution of H_2S (98.9–97.9) and CO_2 (0.16–0.32).

Liquid products of thermal decomposition of *D,L*-Met were evaluated by means of the chromatomass spectrometry (Table 3).

Composition of the decomposition products formed and the values of activation energy of the process tell that the cleavage of C–C and C–S bonds takes place. It is accompanied by formation of such products as CO_2, CH_3SH, and H_2S. Important role probably play the intramolecular cyclization products leading to formation of methylthiazole, methylthiazolidine, and the pyridine and thiophene derivatives. The C–N bond is not exposed to cleavage in the processes of decomposition of the amino acids. It is proved by the absence of a significant amount of NH_3 in the reaction products.

Decomposition of *D,L*-Met, *L*-Cys, and *L*-Cys_2 in the course of 20–40 min at the temperatures above 200°C is accompanied by the formation of sulfur-containing gaseous product and liquid nitrogen-containing eterocyclic compounds which are unwanted

Table 3. Results of chromatomass spectrometric analysis of liquid products of thermal decomposition of *D,L*-Met at 240°C

Product	Yield, mol %
3-methylthio-1-propanamine	75.66
Methanethiol	14.42
2-Propen-1-amine	4.84
Dimethylpyridine	1.20
Methylpyridine	0.76
Dimethyl disulfide	0.59
Thiophene	0.88
Pyridine	0.75
2-Propen-2-methyl-1-amine	0.41
Methylthiopropane	0.05
1,2-Propanodithiol	0.04

in the course of thermal treatment of the protein-containing foodstuffs. Formally the rate of the overall process at low degree of decomposition of the starting compounds (30–50%) is described by the kinetic equation of the first order reaction. Despite of close values of the apparent activation energies of thermodecomposition of *D,L*-methionine, *L*-cysteine, and *L*-cystine (195, 193, and 184 kJ mol^{-1} respectively) the effective rate constants at one and the same temperature differ by one or two orders of magnitude in the above-mentioned series.

EXPERIMENTAL

DTA analysis of amino acids was carried out on a Paulik-Paulik-Erdey derivatograph at the heating rate 10°C/min. Mass spectrometric analysis of the gaseous thermodecomposition products was carried out on a MI 1201 mass spectrometer with the ionizing electron energy 70 eV. Liquid products were analysed on a FOCUS DSQ chromatomass spectrometer with the 60000×0.25 mm capillary TR 5 column. The injector temperature 250°C. Helium carrier gas flow 1 ml min^{-1}. The column temperature varied from 50 to 250°C. Mass spectra were registered in the mass number range 29–500. The products were identified by comparison of their mass spectra with the data from the NIST 2003 electronic library.

Crystalline *D,L*-Met of the "chemically pure" grade, and *L*-Cys and *L*-Cys_2 of the "pure" grade were used.

The rate of thermal decomposition of the amino acids was studied under static conditions. Scheme of the laboratory installation is presented in Fig. 3.

A weighted sample of the amino acid (20–30 mg) was placed in a glass reactor *1* with the about 35 cm^3 volume. The system was evacuated (*p* 1 mm Hg), and the reactor was sealed. Equality of pressure in the reactor *1* and the compensational chamber *4* was

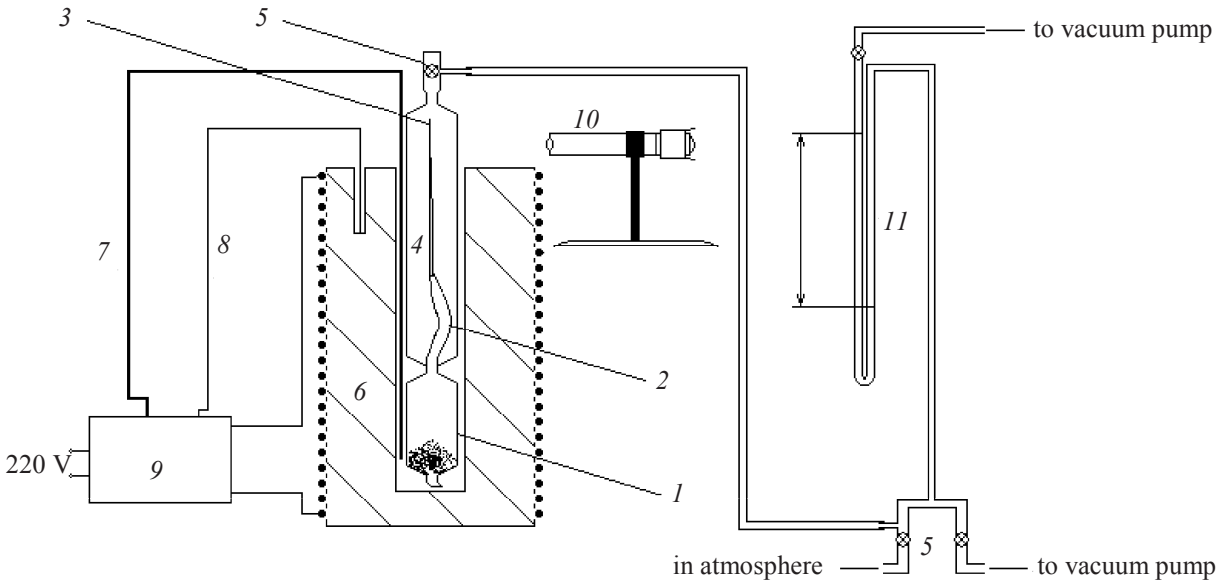

Fig. 3. Scheme of the laboratory installation for the study of kinetics of thermal decomposition of the sulfur-containing amino acids: (*1*) reactor, (*2*) membrane, (*3*) membrane pointer, (*4*) compensational zone, (*5*) stopcocks, (*6*) thermostate, (*7*) setting thermocouple, (*8*) reference thermocouple, (*9*) thermoregulator, (*10*) eyepiece, and (*11*) mercury manometer.

provided with the help of fluoroplastic cockes *5*. Equality of pressure in the reactor and in the compensational chamber was indicated by the position of the pointer *3* connected with the membrane *2*. Position of pointer on the zero point was established with the help of eyepiece *10*. The thermostating block *6* was equipped with the setting *7* and the reference *8* thermocouples connected with the thermoregulator *9*. Pressure of gases liberating during the decomposition was measured by means of the mercury manometer *11*. Rigidly fixed reactor was plunged in the thermostating block with the given temperature. The moment of achievement of this temperature by the reactor was accepted as the zero point of metering of thermal decomposition of the amino acid.

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