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Kinetics of Heat-Induced Transformation of Copper Complexes with Amino Acids

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Abstract—We have studied the effect of substituent R on the rate and mechanism of thermal decomposition of copper(II) complexes with L-α-amino acids anions $H_2NCH(R)COO^-$. The homolytic decomposition rate increases in the series of CuL_2 complexes with alanine, glycine, valine, isoleucine, leucine, phenylalanine, and serine. Intramolecular redox formation of $^{\bullet+}$CuGly cation-radical upon reduction of Cu(II) to Cu(I) and oxidation of $H_2NCH_2COO^-$ into $H_2NCH_2COO^{\bullet}$ carboxylamine radical is the primary stage of heat-induced decomposition.

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When inorganic salts including those of heavy metals get into living organism metal complexes with amino acids are formed. Such compounds are somewhat dangerous when retained in heat-treated protein food. Therefore the elucidation of their thermal decomposition mechanism and rate is of practical and fundamental interest.

The decomposition of crystalline amino acids salts have been studied mainly by means of differential thermal analysis [1, 2]. Products and suggested mechanism of thermal decomposition of copper glycinate have been discussed in [3].

In this work, we studied the effect of substituent R on mechanism and rate of heat-induced decomposition of copper(II) complexes with anions of L-α-amino acids $H_2NCH(R)COO^-$ (L). The model series included CuL_2 complexes with glycine, alanine, valine, leucine, isoleucine, phenylalanine, and serine. The complexes were prepared via reaction of the corresponding L-α-amino acids (Merck) with copper hydroxide [2].

$$H_2NCH(R)COOH + Cu(OH)_2 \rightarrow Cu[H_2NCH(R)COO]_2 + 2H_2O.$$

In the cases of crystal hydrate formation, water was removed in a vacuum (150°C, 2×10^{-2} mm Hg). Anhydrous complexes contained 99.5% of the main component.

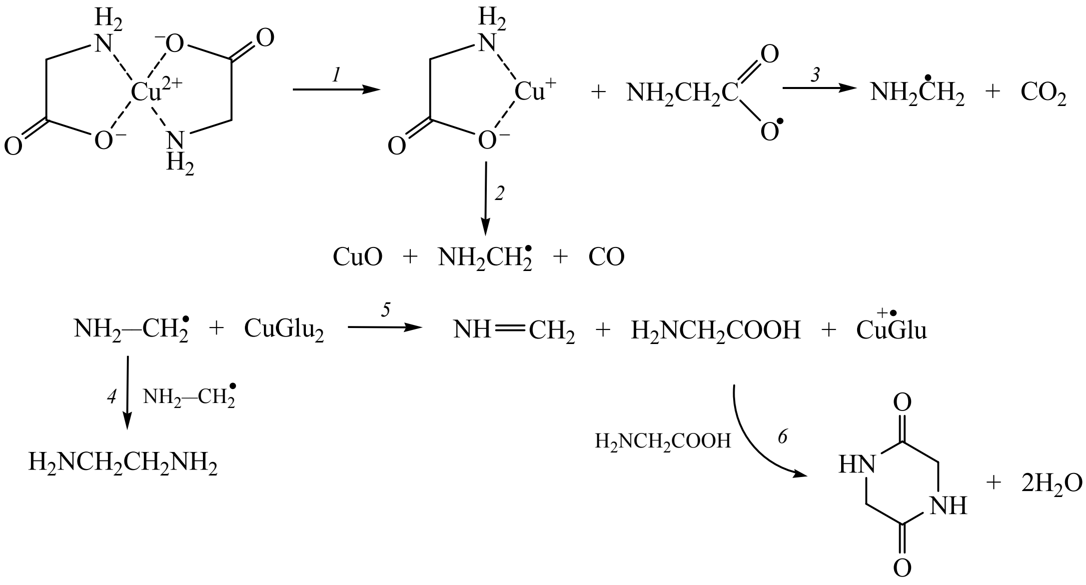
Reaction rate was measured following the pressure of evolved gaseous products in time (glass vacuum manometer system of constant volume) [4].

The composition of volatile products of the thermal decomposition of complexes was studied using the DSQII mass spectrometer. To do so, a specimen of anhydrous metal complex was put into the Eppendorf test tube that was immersed into the ion source of the spectrometer via lock chamber. The tube was heated at a rate 100 deg/min to the complex decomposition temperature (determined separately for each complex). Electron impact mass spectra were recorded each 0.5 s at mass range of 14–400.

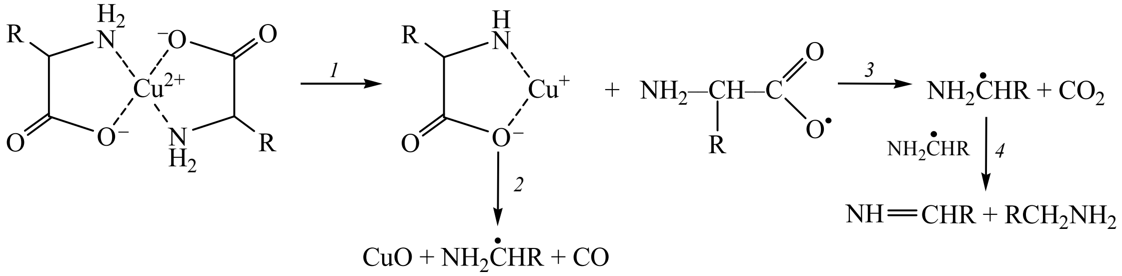
Mass spectra of decomposition products of copper(II) glycinate $CuGly_2$ were recorded under isothermal conditions at 250°C. The following products were identified: CO, CO_2, ethane-1,2-diamine, $HN=CH_2$, glycine, and diketopiperazine. In the initial stages of decomposition the volatile products consisted of CO_2 and CO, thus indicating the radical pathway of heat-induced transformation of the complex. The described mechanism coincided with the data reported in [3]. The metal complex participated in intramolecular redox process to give $^{\bullet+}$CuGly ion-radical and $H_2NCH_2COO^{\bullet}$ carboxylamine radical (Scheme 1, reaction *1*).

Further transformation of the formed radicals occurred via two pathways. Decomposition of $^{\bullet+}$CuGly ion-radical (reaction *2*) led to black CuO powder, CO, and methylamine radical. Carboxylamine radical $H_2NCH_2COO^{\bullet}$ was involved in typical decarboxylation process to give methylamine radical and CO_2 (reaction *3*).

Scheme 1.



Scheme 2.



Methylamine radicals participated in reactions *5* (chain propagation) and *4* (recombination). Glycine was seemingly formed via attack of H_2NCH_2 radical on crystalline copper(II) glycinate (reaction *5*), whereas diketopiperazine formation was likely due to heterolytic dehydration (reaction *6*). The absence of methylamine ion peaks in the mass spectra showed that H_2NCH_2 radicals did not participate in disproportionation reaction.

Reactions *1–3* (Scheme 2) were typical of $CuAla_2$ (270°C), $CuLeu_2$ (240°C), $CuPhe_2$ (230°C), and $CuSer_2$ (200°C). Bulky H_2NCHR radicals disappeared via disproportionation (Scheme 2, reaction *4*) rather than by recombination.

CO, CO_2, alkylimine RCH=NH, and alkylamine RNH_2 were identified among the volatile decomposition products. Signals of the corresponding amino acids, diketopiperazine derivatives, and H_2NCHR recombination products were absent in the mass spectra; alkylamine radicals underwent the disproportionation reaction.

The kinetic curves of increase in the pressure of volatile products during $CuAla_2$ decomposition are shown in the figure. The induction period was followed by active decomposition of the metal complex, the latter being formally described by the first-order rate law. From that part of the curves we determined the effective rate constants (k) and energy parameters of the overall process.

Similarly, we investigated kinetics of decomposition of all the studied complexes and calculated kinetic and activation parameters of the reactions (see the table).

Utilizing the Arrhenius equation, we calculated the effective rate constants of thermal decomposition at 230°C. The results show that the reactivity of the metal complexes increased in the following series: $CuAla_2 < CuGly_2 < CuVal_2 < CuIle_2 < CuLeu_2 < CuPhe_2 < CuSer_2$.

In the case of glycine complex the thermal decomposition occurred via chain radical process (Scheme 1);

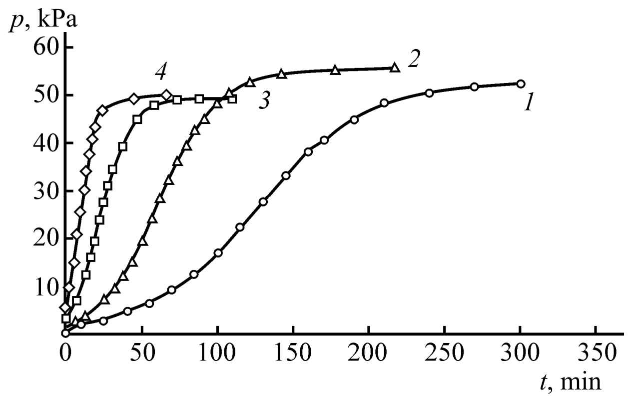
Kinetic parameters of thermal decomposition of Cu[$H_2NCH(R)COO]_2$ complexes

R	T, °C	$k_R \times 10^5$, s^{-1}	$k_{230} \times 10^5$,[a] s^{-1}	E, kJ/mol	ln k_0	R	T, °C	$k_R \times 10^5$, s^{-1}	$k_{230} \times 10^5$,[a] s^{-1}	E, kJ/mol	ln k_0
H	230 236 241 246	12.0 45.0 56.8 131	13.9	307	64.7	$(CH_3)_2CHCH_2$	218 224 231 239	18.7 36.8 64.9 83.1	51.0	148	27.8
CH_3	244 250 262 258 268	20.2 25.5 61.4 35.0 124	5.6	170	30.9	$CH_3(C_2H_5)CH$	222 228 234 244	9.2 16.0 33.1 49.4	18.9	174	32.9
$(CH_3)_2CH$	225 231 238 245	13.2 16.3 30.8 55.2	17.4	159	29.4	$C_6H_5CH_2$	207 212 228 238	6.5 30.6 179 690	219	311	68.4
						$HOCH_2$	159 167 173 182 192	8.8 15.5 26.7 30.2 93.6	702	112	21.7

[a] The rate constants were calculated using the Arrhenius equation.

in the case of substituted metal complexes Cu[H_2NCH·(R)COO]$_2$, the rate-limiting stage was intramolecular redox reaction of homolytic rupture of metal–oxygen bond (Scheme 2). In this reaction copper(II) ion acted as oxidizer and the amino acid anion was a reducing agent. Electron density drift in the metal complex was accompanied by generation of $^{\bullet +}$Cu[$H_2NCH(R)COO$] ion-radical and $H_2NCH(R)COO^{\bullet}$ radical that were then rapidly decomposed with CO_2 and CO elimination.

The rate of bond homolysis in the metal complex was directly proportional to the stability of the formed free radicals. The stability of the radicals was due to bulky alkyl groups in substituent R.



Kinetics of change in the pressure of volatile products of $CuAla_2$ decomposition at, °C: (*1*) 244, (*2*) 250, (*3*) 262, and (*4*) 268.

The high reactivity of $CuSer_2$ could be due to the presence of electron-acceptor $HOCH_2$ groups in the side chain, these groups could form additional hydrogen bonds with the neighboring molecules.

It should be noted in conclusion that the use of the first-order kinetic equation to describe the solid-phase process is a common approach to quantify the metal complex reactivity. The complicated set of parallel and sequential elementary stages followed a simple kinetic equation, therefore it was reasonable to assume that the rate of transformation was limited by reactions *1* and *5* (Scheme 1) in the case of copper glycinate and by reaction *1* (Scheme 2) in the cases of the other complexes.

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