Calculation of structure and spectra of the glycine radical with dehydrogenated carboxyl group

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Summary. A new type of glycine radical with the dehydrogenated carboxyl group (so far unknown) has been detected by electrochemical methods on Pt electrode and studied by quantum chemical methods in gas phase, solvents and on the surfaces of metal clusters. The structure, conformational behavior, electron paramagnetic resonance (EPR) and infra-red (IR) spectra of this glycine radical in two isomeric forms and a number of other well-known carbon-cenetered and nitrogen-cenetered glycine radicals have been studied by density functional theory (DFT) with linear response (LR) and quadratic response (QR) technique. Spin catalysis of oxidative decarboxylation of glycine on platinum and copper surfaces and some other magnetic phenomena in decay of amino acids are discussed.

Keywords: glycine radical, triplet state of dyes, carboxyl group, asymmetric vibrations.

Introduction. Amino acids are among the most important building blocks of life. Glycine is the simplest of amino acids; thus it surves as an important model compound in biophysics and biochemistry of proteins. As such model, glycine, its ions and radicals are widely studied both experimentally and theoretically during last decade [1-9]. In the course of our studies of electrochemical oxidation of glycine (and other amino acids) on platinum electrode in alkaline solvents we have detected some transient species, which have been assigned as ions and radicals on the ground of quantum chemical calculations. This theoretical study provides new type of radicals which have to be analized in the context of previous numerous findings.

Different glycine radicals produced by high-energy irradiation of solid glycine have been studied in a great number of EPR researchs since the begining of EPR era [10]. Most of the studies have focused their attention on the carbon-centered glycine radical $NH_2-CH^{\bullet}COOH$, which is one of the most important γ-radiation products of glycine in solvents and solids [1, 3-6, 11, 12]. Though the transient species from irradiated glycine are known during half a century [5, 11], the importance of some protein radicals has been appreciated quite recently when it had been found that they are involved in enzymes activity [13, 14]. The carbon-centered glycine radical formed during activation of ribonucleotide reductase has been thoroughly investigated by EPR and by DFT methods [1, 3, 6, 12, 14]. This carbon centered glycine radical was first observed in γ-irradiated crystalline glycine in 1959 [5] and later was studied by EPR and electron nuclear double resonance (ENDOR) methods [1, 11] with detailed theoretical interpretation of hyper-fine structure of magnetic resonances [1-3, 6, 9, 12]. Similar results were obtained in solvents; the OH radical produced in the radiolysis of water is assumed to attack aliphatic amino acids predominantly at the C_a position by abstracting of a hydrogen atom from the C-H bonds [5].

Besides these physical studies of structure

and magnetic properties of the C-centered glycine radical, a number of photochemical and electrochemical investigations have been devoted to reactivity of glycine and of the intermediates produced in the course of its dissociation [5, 15-17]. In fact the oxidative decarboxylation of amino acids is intriguing biochemists during the whole century [15]. The mechanism of the OH-induced decarboxylation of the simple amino acids in the anionic form was studied in pulse radiolysis experiments [5, 15]. These studies for glycine have shown that the aminium radical ($NH_2^{\bullet+}$-CH_2-COO^-) and aminyl radical ($NH^{\bullet}$-CH_2-COO^-) were formed. The aminyl radical suffered slow homolysis of the C-C bond liberating COO^-, whereas the the aminium radical undervent a very fast heterolytic C-C cleavage to produce carbon dioxide [15]. Radiolysis of amino acids in dilute aqueous solutions have indicated that the hydrated electron adds to the carboxyl group [6, 11]. On the other hand, the photooxidation of amines themselves provides a great deal of information about the properties and reactions of aminium and aminyl radicals [15]. However the information about radicals derived from simple amino acids like glycine is scarce. In photosensensitized oxidation and in photoinduced decarboxylation of glycine (and its derivatives) in a number of solvents the involvement of the aminium radical have been proposed [5]. In these experiments the mechanism of the process has been attributed to a reductive quenching, in which an electron is transferred from the nitrogen lone pair of amino acid to the photosensitizer. Since amines are known as good quenchers of excited states in photochemistry (the metastable triplet state of dyes, or the singlet state of dioxygen) [18] the first step in the process is attributed to electron-transfer and the aminium radical formation [15, 19]. The aminium radical undergoes deprotonation either from the α C-H group, or from the N-H group (in primary and secondary amines); the latter process yields aminyl radical, which is a strong oxidizer [15].

Quenching of 4-carboxybenzophenone (CB) excited to the triplet state ($^3CB^*$) by amino acid anions of the general formula NR_2-CH_2-COO^- in basic aqueous solutions have been studied recently [15, 19]. It was shown that the major quenching process is an electron transfer to triplet $^3CB^*$ producing the $CB^{\bullet-}$ anion radical and the $NR_2^{\bullet+}$-CH_2-COO^- aminium radical. For glycine the initial geminate product to the $CB^{\bullet-}$ anion radical is the radical $NH_2^{\bullet+}$-CH_2-COO^-, which is inherently oxidizing. This radical is expected to have a short lifetime since it tends to decarboxylation [15]:

$NH_2^{\bullet+}$-CH_2-$COO- \rightarrow NH_2$-$^{\bullet}CH_2 + CO_2$
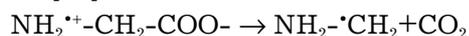
The α-aminomethyl radical NH_2-$^{\bullet}CH_2$ from the decarboxylation process is strongly reducing and even able to reduce CB ground state. Such reducing character of the α-aminomethyl and α-aminoalkyl radicals has been established in chemical reactions [15] and in electro-chemical studies of transient carbon-centered radicals produced by modulated photolysis with phase-sensitive voltammetry [20].

In this short review of possible radicals and ions derived from glycine we have to mention collisional activated dissociation spectra of the glycine radical cation [7, 21]. Possible mechanisms of fragmentation products found in the glycine mass spectrum have been anaized recently [21]. The dominant fragmentation process arises from the C-C cleavage by abstracting carboxylic group, which corresponds to the immonium cation NH_2-CH_2^+ the mass charge ratio m/z=30 peak is quite prominent [21]. This cation is the most abundant fragment in vacuum UV photoionization mass spectra of alanine [7] and of other amino acids [7, 21]. The mass spectrometry of glycyl radical cation is the most relevant and important technique for comparison with analysis of electrochemical oxidation of glycine. In this work we shall try to cover the more probable subsequent ionization and dissociation channels postultaed in chronopotenciometric study of electrooxidation of glycine [22]. Previous investigation [22] was based on semi-empirical PM3 calculations and need to be verified on the ground of more sophisticated methods and modern computational technology.

Methods. Density functional theory (DFT) with the B3LYP functional is used throughout the paper. All molecular structures and harmonic vibrational frequencies, including those of the starting anion of aminoacetic acid, glycine radicals and radical-cations, are herein calculated using the UB3LYP method implemented in

Gaussian 03 program [23]. The 6-31 G(d,p) basis set [24] is used for geometry optimization and the single-point recalculated energy at the 6-31++G(d,p) and 6-311++G(3df, 3pd) basis sets [23, 24], based on optimized structure, are used for termochemical estimations. We used these basis sets for light atoms and the SDD basis set of the Schtutgard group [25] for calculation of metals and complexes on metal clusters.

The UB3LYP/6-31G(d) harmonic vibrational frequencies, scaled by 0.96, were used for analysis of IR absorption and Raman scattering spectra and also for the correction of zeropoint vibrational energy (ZPVE). Magnetic EPR properties of radicals are calculated by two methods. Hyperfine coupling (HFC) constants are calculated by DFT UB3LYP approach. The g-factor tensors and the singlet-triplet transition probability are evaluated by linear response (LR) [26] and quadratic response [27] (QR) techiques, respectively, in the frame work of multiconfiguration self-consistent field (MCSCF) method [28]. Similar LR and QR calculations are performed in the framework of DFT method [29].

In the present paper we discuss structure of radicals detected in the course of our studies of electrochemical oxidation of glycine on platinum electrode in alkaline solvents (pH=11-12). The chronopotenciometric analytical method with the controlled current and voltamperometry with linear development of potential are used [22]. It was established that electrooxidation of glycine on platinum electrode occurs irreversibly in alkaline solution and represents the manystep process. The calculated kinetic parameters indicate that the mechanism of the studied electrooxidation is dependent in a great extent on the concentration, temperature of solvent, velocity of potential application and the nature of background.

Voltammetry curves of the aqueous solution of glycine at the 0.5 M Na_2SO_4 background indicates that electrooxidation occurs in alkaline solvents starting with pH=9. Voltammetric temperature dependence was measured in the interval 283-333 K.

Results and discussion. Voltammetry curve of the 0.1 M glycine solution (pH=12, υ -0.05 V/s) shows (Fig. 1) a maximum at 1.9 V which indicates a discharge of the amino acid ($E_{1/2}$=1.6 V). It
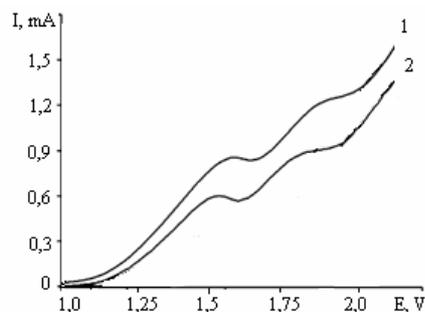

Fig. 1. Potentiodynamic curve of glycine electro-oxidation on platinum electrode in water solution (pH=12, υ=5·10⁻² V/s, T=295 К, background 0.5 M Na_2SO_4): 1. $C_{(glycine)}$=0.1 M. 2. $C_{(glycine)}$=0.075 M.

starts to grow at about +1.1 V. An increase of glycine concentration leads to the higher maximum current at the same potential, which indicates electrochemical oxidation of glycine [22]. In the absence of glycine the oxygen evolution is observed from +0.6 V, which is attributed to the enhanced overpotential of oxygen evolution at the pretreated Pt electrode. The addition of glycine to the solvent induces an anodic peak, indicating that the oxygen evolution current is supressed by the adsorption of glycine anions NH_2-CH_2-COO^- that exist predominantly at this pH in alkaline solvents [16].

With our high concentration of glycine the limiting process is adsorption, since all molecules penetrate the double-electric layer at this potential. In electrochemical study of Ogura et al. [16] much lower concantration (about 0.001 M) is used; in this case the limiting process is desorption, since the double-electric layer is quite dense. As a result, the anodic peak decreases with increasing concentration of amino acid in experiment of Ogura et al. [16].

Small peaks at the voltammetry curve near E=2.1 V can be attributed to ionization (Fig. 1). Since glycine is adsorbed on platinum from the solvent in a form of anion, we can propose that the discharge and the corresponding first ionization of the anion NH_2-CH_2-COO^- provides a transient radical, which is identified as NH_2-$^\bullet CH_2$-CO_2 on the ground of our DFT calculations. This is not the same C-centered radical which is obained in the irradiated glycine and which is very popular in numerous theoretical and EPR studies [1, 3-6, 11, 12]. The late is produced by abstraction of hydrogen atom from the C-H
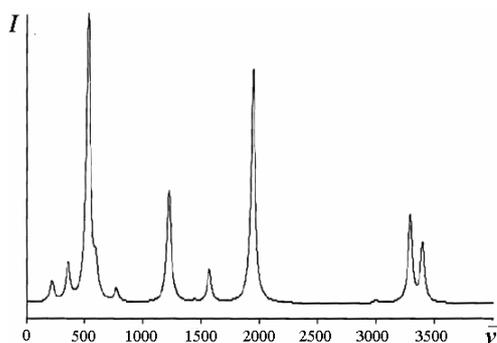
Fig. 2. IR spectrum of the radical NH_2-CH_2·COO calculated by B3LYP/6-31 G method (υ — wave numbers, cm^{-1}, I — Intensity km/mol).
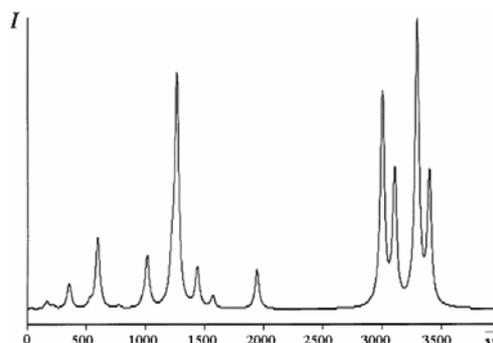
Fig. 3. Raman spectrum of the radical NH_2-CH_2·COO calculated by B3LYP/6-31 G method (υ — wave numbers, cm^{-1}, I — Intensity km/mol).

bond in reaction with OH radical, induced during the γ-radiolysis of water [11].

In our case the anion NH_2-CH_2-COO^- is adsorbed on the Pt surface by the COO^- group (see next section) and discharge occurs through its ionization. What can happen with the obtained radical of the brutto form NH_2-CH_2-CO_2? Ogura et al. [16] proposed that decarboxylation starts immidiately.

At this point we need to consider the structure of the radical of the brutto form NH_2-CH_2-CO_2 in more details. It is a glycine radical with the dehydrogenated carboxyl group. Such radical can exist in two forms: oxygen-centered radical species NH_2-CH_2-$COO^•$, which have been calculated by Yu at el. [4] with a short C-C bond distance (1.535 Å) and the $CH_2^•$-centered radical with a long C-C distance [22]. As follows from our present calculation in vacuum the former O-centered radical has a total energy equal to -283.76415 hartree (6-31 G**); spin density (ρ) is concentrated on two oxygen atoms (0.55 and

0.35). The late radical in vaccum is a weak complex between NH_2-CH_2 species and the carbon dioxide molecule being in a nonlinear form. Results of geometry optimization strongly depend on the basis set chosen. The best results, when all vibrational frequencies are real, has been obtained with the 6-31+G basis set: R(C-C)=2.27 Å, spin density is concentrated on the NH_2-CH_2 species ρ_C=0.59, ρ_N=0.23, ρ_O=0.1. An important feature of this radical in all calculations is that carbon dioxide is not a free molecule in such an associate. The O-C-O angle varies from 142 till 170° depending on basis set and the C-C distance can be as long as 3.01 Å. It is probably difficult to detect such radical in gas phase, but it becomes much more stable in polar solvent. We get shorter C-C distance for the NH_2-CH_2-CO_2 radical (2.02 Å) upon geometry optimization in water with the polarized continuum model (Table 1). In Fig. 2 the calculated IR spectrum of the radical NH_2-$•CH_2$-CO_2 is given. All calculated vibrational frequencies of the

Table 1

Structural and spin-density parameters of the radical NH_2-CH_2-CO_2 in the $^2A'$ ground state, calculated in water solvent by PCM B3LYP/6-31G** approach (hyperfine coupling parameters are in MHz, bond lengths are in Å)

Atom (A)	ρ_A	a_A^{iso}	$B_A^{x,x}$	$B_A^{y,y}$	$B_A^{z,z}$	Q_A	A-B^a	R $_{A-B}$
C_1	0.329	39.62	-28.30	-26.77	55.08	-0.150	1-2	2.026
C_2	0.130	5.69	-12.80	-8.55	21.36	0.581	1-5	1.355
O_3	0.111	-18.35	20.15	19.49	-39.64	-0.489	2-3	1.206
O_4	0.143	-30.93	25.69	25.23	-50.92	-0.464	2-4	1.210
N_5	0.302	16.90	-13.77	-13.56	27.33	-0.493	5-7	1.019
$H_{6,7}$	-0.009	-17.71	-18.33	-4.13	22.47	0.335	5-6	1.019
$H_{8,9}$	0.001	11.81	-14.72	-0.64	15.37	0.173	1-8.9	1.087

^{a} Bond angles: OCO=146.8°, CCN=113.6°, CCO$_4$=104°, CCO$_3$=109°
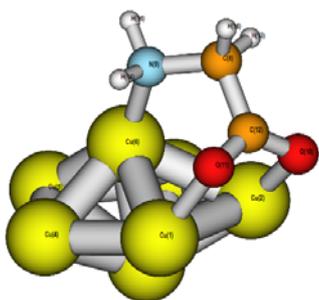
Fig. 4. The calculated model of the NH_2-CH_2•COO radical adsorption on the Cu_7 cluster.

Fig. 5. The calculated model of the NH_2-CH_2•COO radical adsorption on the Au_3 cluster.

radical are real; the lowest wave number $v_1=26$ cm^{-1}, which is close to microwave revion, corresponds to twist of the whole species. Two low-frequency IR bands (Fig. 2) at 227 and 371 cm^{-1} correspond to C-C stretching in combination with the OCO and CCO bending. Their relatively high intensity (54 and 97 km/mol, respectively) indicates specific character of the weak C-C bond. The most intense IR band at 548 cm^{-1} corresponds to NH_2 wag (864 km/mol) and a band around 1920 cm^{-1} is produced by asymmetric vibrations of the CO_2 group. In-phase C-O vibrations being out-of-phase with the C-N stretch provides IR band at 1218 cm^{-1} with middle intensity (332 km/mol), while the total in-phase counterpart at 1258 cm^{-1} provides an intense Raman scattering (Fig. 3).

In spite of the long C-C distance, the spin density is delocalized ($\rho_N=0.3$, $\rho_{C1}=0.33$) with large nonpaired electron spin density on CO_2 moiety ($\rho_{COO}=0.38$, Table 1). Some small spin polarization on the CH_2 protones ($\rho_H=-0.01$) provides essential hyperfine coupling (HFC) constants. The largest isotropic HFC constant is on the ^{13}C nucleus of the CH_2 group ($a_C=39.6$ MHz). Considerable isotropic HFC parameters are predicted for the ^{17}O nuclei $a_{O(5)}=-30.9$ and $a_{O(4)}=-18.5$ MHz; the anizotropic HFC tensors for these nuclei are also large. In contrast the carboxylic ^{13}C nucleus has a small HFC constant (Table 1). Analysis of anisotropic HFC tensors indicates a large spin density on 2p-AOs of all nuclei (Table 1).

Such peculiar radical, which has not been reported so far, can be found upon electrochemical anodic discharge of glycine in alkalin solvents. From our DFT calculations we have found that the studied radical is strongly stabilized on the surface of metal clusters (Cu, Au, Pt). As an example we present adsorption of the studied
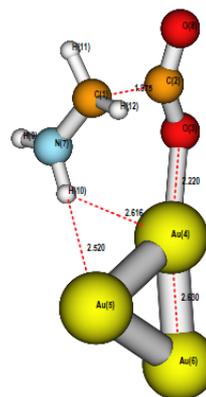
radical on the Cu_7 cluster (Fig. 4) and on the Au_3 cluster (Fig. 5) and Au atom (Fig. 6).

Electron paramagnetic resonance (EPR) is an important experimental tool for physicochemical determination of free radicals generated in proteins. Unfortunately we have no possibility to apply ERR technique to detect the radical which we have calculated and which spectral properties we have predicted. But we hope that the new type of glycine radical proposed to excist in alkalin electrochemical environment could be defected in near future.

We have also calculated the singlet-triplet transition intensity in the long-wave absorption tail of the anion NH_2-CH_2-COO^-, which exists in the alkaline solvent at high pH>9. Our calculation of spin-orbit coupling with the quadratic response method [27-29] by Dalton code [30] provides a relatively high oscillator strength for the $S_0 \rightarrow T_1$ transition at 241 nm (f=0.51x10^{-6}). The T_1 state has the ^{3}A'' spatial symmetry in respect to reflection in the plane of the OCO-CN atoms. The second triplet state T_2 is a totally symmetri-
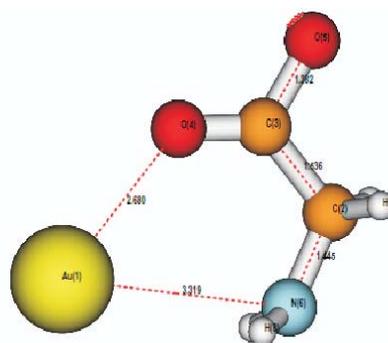

Fig. 6. The calculated model of the NH_2-CH_2•COO radical adsorption on the Au atom.

cal ^{3}A'; the calculated wavelength (220 nm) of the $S_0 \rightarrow T_2$ transition coincides with an intense offset of the singlet-singlet absorption of glycine anion. At the same time the calculated oscillator strength for the $S_0 \rightarrow T_2$ transition (f=0.44x10^{-4}) is comparable with the spin-allowed singlet-singlet transition. For example, the $S_0 \rightarrow T$ absorption of aromatic hydrocarbons is five-six orders of magnitude weaker [28]. These results mean that relativistic effects are important for the near-UV light absorption by the simple amino acides. One can not exclude that similar effects could be important for polypeptides and real proteins. Thus radiation damage to the simple amino acides, like glycine, can be induced at longer wavelength, than it was generally accepted and which it is known from their typical absorption spectra detected by standard spectrophotometer [31-32]. The $S_0 \rightarrow T$ absorption of amino acides has not been detected so far; this can be done by the Zeemen effect study in molecular crystals.

Conclusion. Analysis of voltammetry curves and quantum chemical calculations indicate that electrochemical oxidation of glycine proceeds in two steps (there are two waves on voltammetry curves) from the adsorbed state and is limited by ionization of the adsorbed molecule for remove of the first electron. The obtained radical NH_2-$^\bullet CH_2$-CO_2 easily undergoes decarboxylation and dissociate to the radical NH_2-$^\bullet CH_2$, which in turn can be ionized. The weakly bound NH_2-$^\bullet CH_2$-CO_2 radical is more stable than its electronic isomer known as an oxygen-centered radical species [4]. The $S_0 \rightarrow T$ absorption of glycine and the fine structure of a new radical are the most intriguing predictions of this work. EPR measurements are necessary for such benchmark species, like the NH_2-$^\bullet CH_2$-CO_2 radical with importance for biochemistry, combustion and astrophysical researchs.

Розрахунок структури і спектрів радикалу гліцину з дегідрогенізованою карбоксильною групою

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Резюме. Досліджено новий тип радикалу гліцину з дегідрогенізованою карбоксильною групою. Один із них раніше був вивчений за допомогою електрохімічних методів на платиновому електроді, а також методами квантової хімії в газовій фазі, у розчинах і на поверхні металічних кластерів. Методом теорії функціоналу густини, а також методом багатоконфігураційного самоузгодженого поля (БК СУП) з урахуванням техніки лінійного та квадратичного відгуку встановлено структуру, конформаційну будову, спектри електронного парамагнітного резонансу (ЕПР) та інфрачервоні спектри (ІЧ) цього радикалу в двох ізомерних формах і ряд інших добре відомих радикалів гліцину з радикальним центром на карбоні та нітрогені. Обговорено спіновий каталіз окиснювального декарбоксилювання гліцину на платиновій та мідній поверхнях, а також інші магнітні явища при розпаді амінокислот.

Ключові слова: радикал гліцину, триплетний стан барвників, карбоксильна група, асиметричні коливання.

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