1318 Russian Chemical Bulletin, International Edition, Vol. 56, No. 7, pp. 1318—1324, July, 2007

Photochemistry of salicylate anion in aqueous solution

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Photochemistry of the salicylate anion (HSA^-) in aqueous solutions was studied by optical spectroscopy, fluorescence spectroscopy, and nanosecond laser flash photolysis (XeCl laser, 308 nm). Excitation of this species gives rise to the HSA^- triplet state, $HSA^{\bullet}$ radical, and hydrated electron. The last two species are presumably formed due to the absorption of the second photon by the excited singlet state of the anion. In a neutral medium, the main decay channel of the HSA^- triplet state is triplet-triplet (T-T) annihilation. The $HSA^{\bullet}$ radical decays in recombination, and the hydrated electron reacts mainly with the HSA^- anion.

Key words: salicylic acid, laser flash photolysis, triplet-triplet absorption, two-photon processes, hydrated electron.

Organic carboxylic acids represent a class of compounds abundant in natural waters.[1] These acids are capable of forming complexes with transition metals (including Fe^{III}), whose photochemistry can contribute substantially to the balance of organic compounds in aqueous systems.[2—9] Aromatic carboxylic acids have their own intense absorption bands in the UV spectral range and in the non-coordinated state they can undergo photochemical transformations under solar irradiation.

Salicylic acid (2-hydroxybenzoic acid) (H_2SA) and its derivatives are considered as representatives of the complexing functional groups in humic substances[10] and can serve as model compounds demonstrating the photochemical properties of natural hydroxy acids. It is known that the H_2SA derivatives luminesce in the blue spectral region[11—15]; however, the photochemical properties of these molecules are poorly studied. In the very recent study,[12] the triplet-triplet absorption spectra of a series of H_2SA derivatives in organic solvents have been detected by laser flash photolysis. In our previous works,[16,17] the photochemistry of 5-sulfosalicylic acid (H_3SSA) was studied in neutral aqueous solutions. Under these conditions, the major form of H_3SSA was the dianion ($HSSA^{2-}$). Excitation (XeCl laser, 308 nm) of $HSSA^{2-}$ produces the triplet state of the dianion, hydrated electron (e_{eq}^-), and $HSSA^{\bullet -}$ radical anion. The last two species are generated due to two-photon processes.

In this work, we studied the photochemical properties of the salicylate dianion (HSA^-) in the framework of the program of investigation of phototransformations of organic compounds in natural water. This species is the major photoactive form of the acid in the pH range characteristic of natural water. Considerable attention is given to the determination of the spectral and kinetic characteristics of the primary intermediate states and species generated by HSA^- photoexcitation.

Experimental

Sodium salicylate ($\geq$99.5%, Fluka) was used without additional purification. Solutions were prepared with doubly distilled water. Unless otherwise specified, all experiments were carried out with deoxygenated samples in the cell with an optical path length of 1 cm at 298 K. Argon was purged through the solutions to remove oxygen.

A laser flash photolysis setup using excitation with an excimer XeCl laser (308 nm) was used (pulse duration 15 ns, irradiation area 0.14 cm^2, energy pulse up to 25 mJ).[16] Absorption spectra were recorded on a Hewlett Packard HP 8453 spectrophotometer. NMR spectra were obtained on a Bruker DPX-200 spectrometer (200 MHz). The pH values of the samples were measured with an Anion-4100 pH-meter.

Fluorescence spectra of deoxygenated solutions were recorded on a Varian CARY Eclipse spectrofluorimeter in the cell with an optical path length of 1 cm. The spectra were corrected[18] to the spectral sensitivity of the instrument using quinine bisulfate in 1 *M* H_2SO_4 as standard. The luminescence quantum yield of H_2SA solutions was determined by an earlier described procedure[19] using quinine bisulfate solution in 1 *M* H_2SO_4 as standard; $\phi = 0.546$. Triplet-triplet absorption of anthracene in benzene (band with the maximum at $\lambda = 431$ nm, absorption coefficient $\varepsilon = 4.2 \cdot 10^4$ L mol^{-1} cm^{-1}, quantum yield of formation $\phi = 0.53$)[20] was used to determine the laser pulse energy. Kinetic curves were calculated by the specially developed program using the fourth-order Runge—Kutta method.

Results and Discussion

Spectroscopy of aqueous solutions of salicylic acid. Salicylic acid bears two mobile protons (H_2SA): for the COOH

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1270—1276, July, 2007.

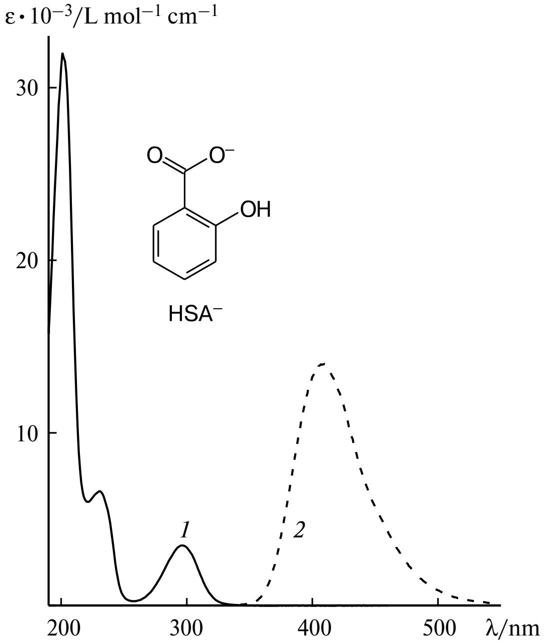

Fig. 1. Absorption (*1*) and luminescence (*2*) spectra of the salicylate anion HSA^- in aqueous solutions at pH 7.

and OH groups pK_a is 3.0 and 13.4, respectively.[21] Thus, in a wide pH range (4—12) the major form of the acid in aqueous solutions is the HSA^- monoanion. The absorption and luminescence spectra of this species are shown in Fig. 1. The presence in the spectrum of the long-wave absorption band with a maximum at 300 nm ($\varepsilon \approx 3.5 \cdot 10^3$ L mol^{-1} cm^{-1})[22,23] corresponding to the π—π^*-transition[24] is characteristic of all H_2SA species. The observed large Stokes shift of HSA^- luminescence (~9300 cm^{-1}) is characteristic of the salicylic acid derivatives and attributed to the intramolecular proton transfer from the hydroxy to carboxy group with formation of tautomeric (or zwitterionic) forms of these compounds in the excited S_1 state.[11—15] The luminescence quantum yield of HSA^- is $\phi_{lum} = 0.34 \pm 0.04$, which makes it possible to determine the rate constant of the radiative process from the S_1 state ($k_{lum} = \phi_{lum}/\tau_{fl} = (8.1 \pm 0.9) \cdot 10^7$ s^{-1}) based on the known fluorescence lifetime of the monoanion ($\tau_{fl} = 4.2$ ns).[15]

Laser flash photolysis of aqueous solutions of HSA^-. Laser pulse excitation (308 nm) of deoxygenated aqueous solutions of HSA^- induces the intermediate absorption consisting of two bands with maxima at 455 and 720 nm (Fig. 2, *a*), which disappear with substantially differed rates (Fig. 2, *b*), indicating the formation of several intermediate species upon the laser pulse. The lifetime of the band at 455 nm decreases substantially in the presence of oxygen or a triplet energy acceptor, *viz.*, 2,2′-dipyridyl, which indicates its belonging to the HSA^- absorption from the T_1 state ($^3HSA^-$). It is known[12] that the triplet-triple absorption band of the neutral form of salicylic acid (H_2SA) in cyclohexane has a maximum at 440 nm. The shift by 15 nm is due to the change in the acidic form (neutral form H_2SA and monoanion HSA^-) and other type of the solvent (water and organic solvent). Studies on pulse radiolysis[25—27] indicate that the broad band with a maximum at 720 nm corresponds to the absorption of the hydrated electron ($\varepsilon^{720} = 1.85 \cdot 10^4$ L mol^{-1} cm^{-1}).

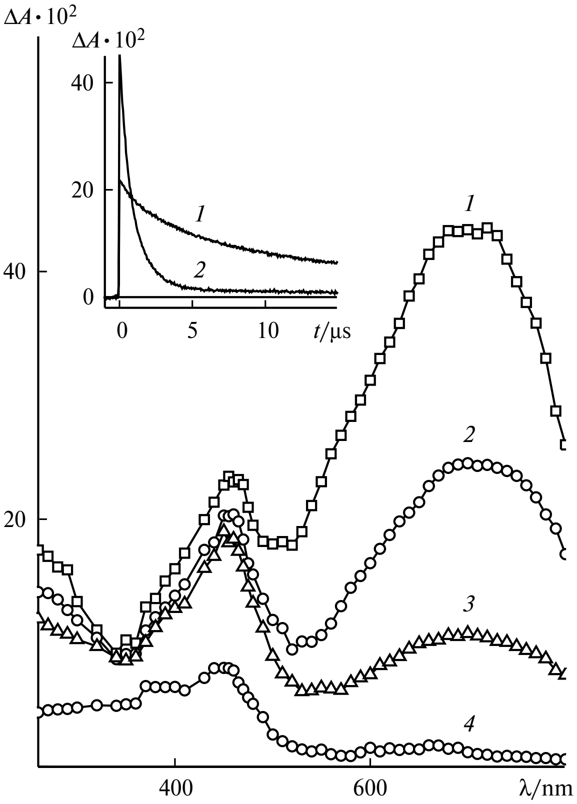

Fig. 2. Transient absorption spectra upon laser flash photolysis of aqueous solutions of HSA^- ($1.7 \cdot 10^{-4}$ mol L^{-1}) at pH 7 in the absence of oxygen 0 (*1*), 0.4 (*2*), 1.2 (*3*), and 10 μs after the laser pulse (*4*). Inset: the kinetic curves at 455 (*1*) and 720 nm (*2*).

The dependence of the yield of the triplet-triplet absorption of HSA^- and absorption of e_{aq}^- on the laser pulse intensity is shown in Fig. 3. The T—T absorption (455 nm) increases linearly at a low intensity and begins to reach saturation at the intensity >100 mJ cm^{-2}. The slope ratio in the initial region of the plot of the $^3HSA^-$ yield *vs* laser pulse intensity (see Fig. 3) determines the value $\varphi(T_1) \cdot \varepsilon_T^{455} = (1.1 \pm 0.1) \cdot 10^3$ L mol^{-1} cm^{-1}, where ε_T^{455} is the absorption coefficient of the $^3HSA^-$ triplet state at 455 nm. The absorption yield at 720 nm is low at low laser pulse intensities and begins to increase substantially in the region >30 mJ cm^{-2}, indicating the two-photon process of hydrated electron generation. The quantum yield of e^-_{aq} at a laser pulse intensity of 200 mJ cm^{-2} is ~8% of the number of all absorbed photons.

In the presence of oxygen in aqueous solutions, e_{aq}^- and $^3HSA^-$ decay rapidly with the characteristic times 50 and 200 ns, respectively. These conditions make it pos-

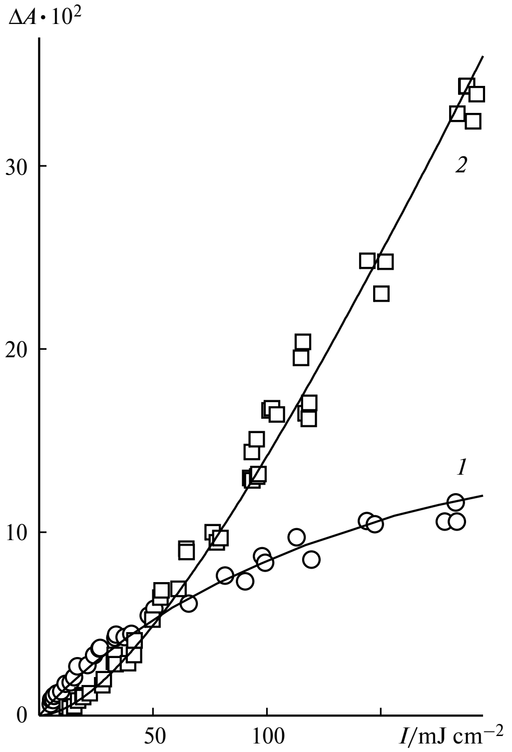

Fig. 3. Plots of the T—T absorbance of the HSA$^-$ anion ($1.2 \cdot 10^{-4}$ mol L^{-1}) in the triplet state (*1*, 455 nm) and the absorbance of the hydrated electron (*2*, 720 nm) *vs* laser pulse intensity at pH 7.

sible to detect one more longer-lived intermediate, whose absorption spectrum consists of two absorption bands with maxima at 390 and 365 nm (Fig. 4). The decay kinetics of this absorption is presented in Fig. 4 (inset). The absorption amplitude at 390 nm (ΔA^{390}) depends on the laser pulse intensity according to the square law and depends linearly on the absorption of the hydrated electron at 720 nm (ΔA^{720}) (Fig. 5). These data indicate that the long-lived intermediate is generated in the two-photon process together with the electron.

In our previous works[16,17] when studying the photochemistry of the sulfosalicylic acid dianion (HSSA^{2-}), we have shown that the two-photon ionization of HSSA^{2-} occurs due to the absorption of the second photon by the excited singlet (S$_1$) state of the dianion to form the hydrated electron—HSSA$^{\bullet -}$ radical anion pair. It can be assumed that, in the case of the salicylic acid anion, photoionization occurs from the S$_1$ state of HSA$^-$ to form the hydrated electron and HSA$^\bullet$ radical. This species refers to radicals of the phenoxy type and can have absorption bands at 370—420 nm,[28—30] which is well consistent with the absorption maxima observed for the long-lived intermediate. The spectrum of the $C_6H_5O^\bullet$ phenoxy radical is presented for comparison in Fig. 4 (see Ref. 28). The linear dependence of ΔA^{390} on ΔA^{720} (see Fig. 5) allows one from the known absorption coefficient of the hydrated electron to determine a similar parameter for the HSA$^\bullet$ radical: $\varepsilon^{390} = (2.5\pm0.3) \cdot 10^3$ L mol^{-1} cm^{-1}. For the phenoxy radicals, the absorption coefficients are arranged in the close interval. For instance, for the $C_6H_5O^\bullet$ radical the absorption band with a maximum at 400 nm has the molar absorption coefficient $\varepsilon^{400} = 2.2 \cdot 10^3$ L mol^{-1} cm^{-1}.[28]

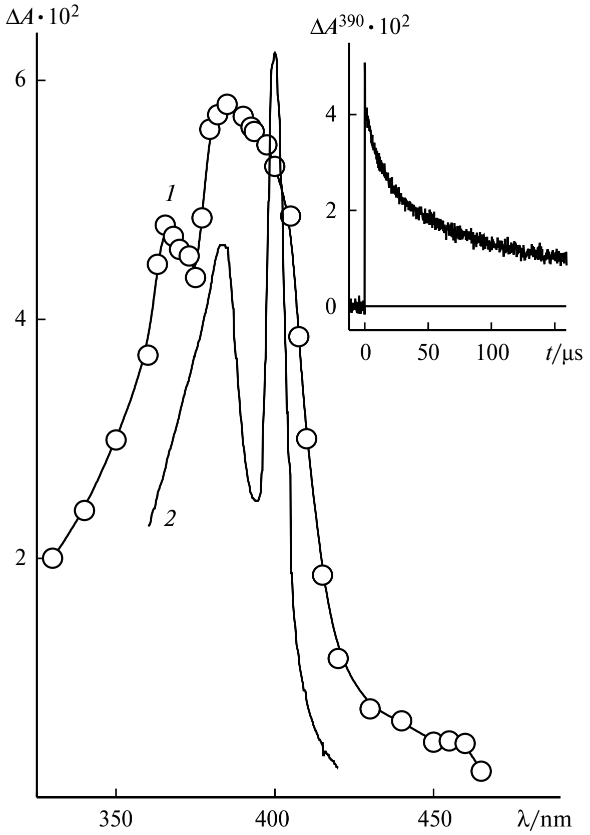

Fig. 4. Transient absorption spectrum of the HSA$^\bullet$ radical 2 μs after the laser pulse (*1*) for oxygen-saturated ([O$_2$] ~10^{-3} mol L^{-1}) aqueous solutions of HSA$^-$ ($1.2 \cdot 10^{-4}$ mol L^{-1}, pH = 10.0) and the absorption spectrum of the phenoxy radical[28] (*2*). Inset: the kinetic curve at 390 nm.

Absorption coefficient of the triplet state of HSA$^-$. The triplet-triplet energy transfer method was used to determine the absorption coefficient from the triplet state of HSA$^-$ ($\varepsilon_T{}^{455}$). 2,2′-Dipyridyl (DP), which has the T—T absorption band with a maximum at 350 nm and absorption coefficient $1.8 \cdot 10^4$ L mol^{-1} cm^{-1},[31] was used as the energy acceptor.

In an aqueous solution of the HSA$^-$ anion with 2,2′-dipyridyl additives, the T—T absorption band of HSA$^-$ (455 nm) appears after a laser pulse. This band rapidly transforms into a new absorption band with a maximum at 350 nm (Fig. 6) belonging to the triplet state of DP (^{3}DP). The kinetic curves of the absorption change at 455 and 350 nm are shown in Fig. 6 (inset). The apparent decay rate constant of the T—T absorption of HSA$^-$ ($k_{app}{}^{455}$) increases with an increase in the dipyridyl con-

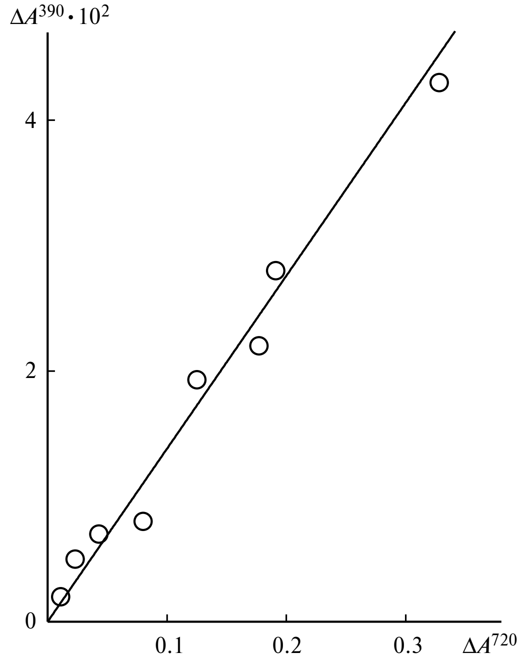

Fig. 5. Plot of the absorption of the HSA$^{\bullet}$ radical (ΔA^{390}) *vs* initial absorption of the hydrated electron (ΔA^{720}) ([HSA$^-$] = $1.2 \cdot 10^{-4}$ mol L^{-1}, pH 10).

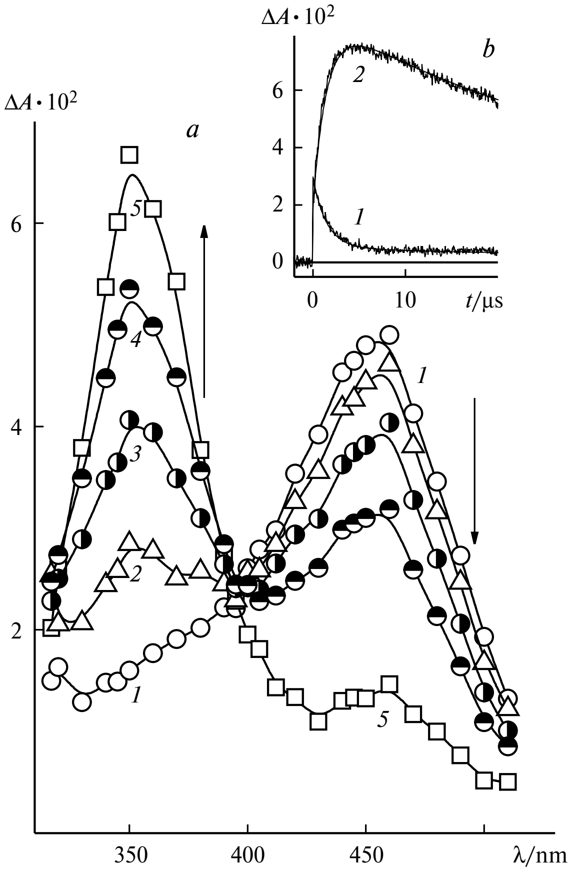

Fig. 6. Transient absorption spectra upon the laser flash photolysis of an aqueous solution of HSA$^-$ ($1.6 \cdot 10^{-4}$ mol L^{-1}) and 2,2′-dipyridyl ($2.4 \cdot 10^{-5}$ mol L^{-1}) (pH 7) 0 (*1*), 0.8 (*2*), 2 (*3*), 4 (*4*), and 14 μs after the laser pulse (*5*). Inset: the kinetic curves of absorption changes at 455 (*1*) and 350 nm (*2*); solid lines are the calculation of the kinetic curves by reactions (*1*)—(*4*) with the parameters indicated in the text.

centration, which confirms the energy transfer process. At low laser pulse intensities (and low initial concentrations of the ^{3}HSA$^-$ triplet), the following kinetic scheme can be used for the description of the experimental kinetic curves and determination of the $\varepsilon_T{}^{455}$ value:

$$^3\mathrm{HSA}^- + \mathrm{DP} \xrightarrow{k_1} \mathrm{HSA}^- + {}^3\mathrm{DP}, \qquad (1)$$

$$^3\mathrm{DP} \xrightarrow{k_2} {}^1\mathrm{DP(S_0)}, \qquad (2)$$

$$^3\mathrm{DP} + {}^3\mathrm{DP} \xrightarrow{k_3} {}^1\mathrm{DP(S_0)} + {}^1\mathrm{DP(S_1)}, \qquad (3)$$

$$^1\mathrm{DP(S_1)} \xrightarrow{\varphi(^3\mathrm{DP})} {}^3\mathrm{DP(T_1)}. \qquad (4)$$

The k_1 constant was determined from the plot of $k_{\mathrm{app}}{}^{455}$ *vs* DP concentration (Fig. 7). The linear dependence of the section cut in the ordinate on the DP concentration results in $k_1 = (4.9\pm0.3) \cdot 10^9$ L mol^{-1} s^{-1}. The rate constants $k_2 = (8.1\pm1.0) \cdot 10^3$ s^{-1} and $k_3 = (1.7\pm0.2) \cdot 10^9$ L mol^{-1} s^{-1} were measured.**[16]** In triplet-triplet annihilation (3), the singlet excited S$_1$ state of DP is generated again and, hence, to calculate the kinetic curve, one should know the quantum yield of the ^{3}DP triplet, which was also measured,**[16]** being $\varphi(^3\mathrm{DP}) = 0.29\pm0.02$.

To determine $\varepsilon_T{}^{455}$ of the T—T absorption band of HSA$^-$, we compared the calculated and experimental kinetic curves at 350 and 455 nm obtained at different initial dipyridyl concentrations and varied laser pulse intensity. The system of differential equations for the set of reactions (1)—(4) was solved to calculate the kinetic curves. The k_1, k_2, and k_3 constants and the ratio of absorption coefficients at 350 and 455 nm for the T—T absorption bands of DP and HSA$^-$ ($\varepsilon_{\mathrm{DP}}{}^{455}/\varepsilon_{\mathrm{DP}}{}^{350} = 0.05$ and $\varepsilon_T{}^{455}/\varepsilon_T{}^{350} = 3.2$) were used as unchanged parameters. The latter were determined from the ratio of amplitudes of the signals at the corresponding wavelengths during laser flash photolysis of separately measured solutions of DP and HSA$^-$. The single varied parameter was the T—T absorption coefficient of HSA$^-$ at 455 nm ($\varepsilon_T{}^{455}$). The obtained value $\varepsilon_T{}^{455} = (7\pm1) \cdot 10^3$ L mol^{-1} cm^{-1} makes it possible to adjust all calculated and experimental kinetic curves. The calculated kinetic curves with the parameters obtained are shown in Fig. 6 (inset) by solid lines.

The product $\varphi(\mathrm{T_1}) \cdot \varepsilon_T{}^{455} = (1.1\pm0.1) \cdot 10^3$ L mol^{-1} cm^{-1} determined above and the found molar absorption coefficient allowed us to calculate the quantum yield of the triplet state of HSA$^-$ ($\varphi(\mathrm{T_1}) = 0.16\pm0.04$). The known lifetime of the S$_1$ state (4.2 ns) and quan-

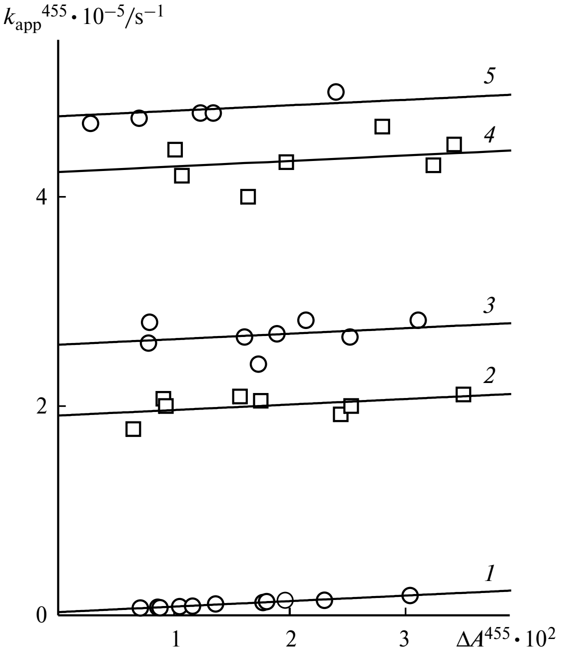

Fig. 7. Plots of the apparent rate constant (k_{app}^{455}) of T—T absorption decay (455 nm) of HSA^- ($1.0 \cdot 10^{-4}$ mol L^{-1}, pH = 7) *vs* signal amplitude (ΔA^{455}) at the concentration $[DP] \cdot 10^5$ = 0 (*1*), 3.5 (*2*), 5.3 (*3*), 8.6 (*4*), and 9.9 mol L^{-1} (*5*).

tum yields of $^3HSA^-$ and fluorescence make it possible to calculate the intersystem crossing (k_{isc} = $(3.7\pm0.9) \cdot 10^7$ s^{-1}) and non-radiative transition $S_1 \to S_0$ (k_{nr} = $(1.2\pm0.2) \cdot 10^8$ s^{-1}) rate constants.

The determination of the photophysical parameters of the HSA^- anion made it possible to calculate the yield of the triplet state and hydrated electron to the end of the laser pulse and estimate the absorption coefficient of the excited S_1 state (ε_{S1}^{308}) at the laser radiation wavelength (308 nm) absorbing the second photon. With allowance for the Gaussian shape of the laser pulse (width 15 ns) and triplet state absorption at 308 nm, the parameter $\varphi(e_{aq}^-) \cdot \varepsilon_{S1}^{308} = (1.6\pm0.3) \cdot 10^3$ L mol^{-1} cm^{-1} describes well the dependence of the yields of $^3HSA^-$ and e_{aq}^- on the laser pulse intensity (see Fig. 3, solid lines). The $\varphi(e_{aq}^-)$ value is the quantum yield of the hydrated electron from the S_N state to which the anion gets after it has absorbed the second photon.[16,17]

Decay reactions of e^-_{aq}, T_1 state of HSA^-, and $HSA^{\bullet}$ radical. ***Hydrated electron e^-_{aq}.*** The apparent decay rate constant of the hydrated electron (k_{app}^{720}) obtained upon the processing of the kinetic curves of electron absorption decay (720 nm) in oxygen-free solutions depends on the initial absorption of e_{aq}^- and the HSA^- concentration (Fig. 8). The section cut in the ordinate by straight lines in Fig. 8 depends linearly on the HSA^- concentration and corresponds to electron capture by the anion

$$e_{aq}^- + HSA^- \longrightarrow HSA^{\bullet 2-}. \qquad (5)$$

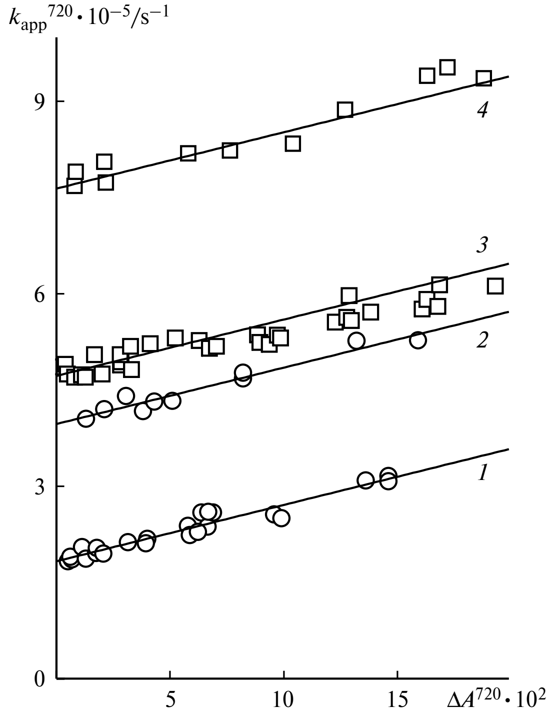

Fig. 8. Plots of the apparent rate constant of absorption decay of the hydrated electron at 720 nm (k_{app}^{720}) *vs* initial signal amplitude (ΔA^{720}) at the concentration $[HSA^-] \cdot 10^5$ = 3.4 (*1*), 7.8 (*2*), 11 (*3*), and 15.5 mol L^{-1} (*4*).

The rate constant $k_5 = (4.6\pm0.2) \cdot 10^9$ L mol^{-1} s^{-1} with allowance for the like charges of the reacting species is close to the diffusion rate constant. The work[32] on pulse radiolysis of aqueous solutions of sodium salicylate gives the rate constant $k_5 \approx 10^{10}$ L mol^{-1} s^{-1}, which is close to the value found by us.

The slope of the straight lines $k_{app}^{720} \propto \Delta A^{720}$ (see Fig. 8) is determined by the second-order reactions

$$e_{aq}^- + e_{aq}^- + 2\,H_2O \longrightarrow 2\,H^{\bullet} + 2\,OH^-, \qquad (6)$$

$$e_{aq}^- + HSA^{\bullet} \longrightarrow HSA^-\,(S_1). \qquad (7)$$

Processing of the kinetic curves for solutions with different HSA^- concentrations provided the total rate constant $k_6 + k_7 = (1.6\pm0.3) \cdot 10^{10}$ L mol^{-1} s^{-1}. It is known from experiments on pulse radiolysis of water[33] that $k_6 = (1.1\pm0.1) \cdot 10^{10}$ L mol^{-1} s^{-1}. Thus, the reaction rate constant for electron capture by the $HSA^{\bullet}$ radical is $k_7 \approx (5.0\pm0.2) \cdot 10^9$ L mol^{-1} s^{-1}, which is also close to the diffusional limit for aqueous solutions.

T_1 State of HSA^-. The lifetime of the triplet state of the HSA^- anion in the presence of oxygen (~$2 \cdot 10^{-4}$ mol L^{-1}) is ~1 μs (pseudo-first-order reaction with O_2 concentration excess). Thus, the quenching constant of the triplet state of HSA^- by oxygen ($k_{O_2} \approx 5 \cdot 10^9$ L mol^{-1} s^{-1}) is close to the diffusion rate constant in water. In solutions containing no oxygen the lifetime of the triplet of HSA^-

increases substantially, and the triplet begins to decay *via* the second-order reaction, which is T—T annihilation

$$^3\mathrm{HSA}^- + {}^3\mathrm{HSA}^- \longrightarrow {}^1\mathrm{HSA}^-(\mathrm{S}_1) + {}^1\mathrm{HSA}^-(\mathrm{S}_0). \qquad (8)$$

In this case, the apparent rate constant ($k_{\mathrm{app}}{}^{455}$) of T—T absorption decay depends linearly on the initial triplet concentration (see Fig. 7, points in line *1*). As a result, the annihilation produces the HSA$^-$ anion in the excited S$_1$ state capable of converting again into the triplet state. Taking into account this effect, the slope (Δ) of line *1* in Fig. 7 is the following:

$$\Delta = 2k_8(1 - \varphi(\mathrm{T}_1)/2). \qquad (9)$$

The quantum yield of the triplet $\varphi(\mathrm{T}_1)$ was determined above and, therefore, these data make it possible to obtain the rate constant value $2k_8 = (3.9\pm0.5)\cdot10^9$ L mol^{-1} s^{-1}. The value of the section cut in the ordinate ($\sim3\cdot10^3$ s^{-1}) corresponds to ^{3}HSA$^-$ triplet quenching by residual oxygen ($\leq2\cdot10^{-6}$ mol L^{-1}) or other uncontrolled admixtures.

Radical HSA•. Phenoxy radicals are known to decay predominantly due to recombination.[34—36] In fact, the decay kinetics of the HSA• radical absorption (390 nm) is well described by the second-order law. The linear dependence of the apparent rate constant ($k_{\mathrm{app}}{}^{390}$) on the absorption amplitude (Fig. 9) makes it possible to determine the recombination rate constant of the HSA• radicals: $2k_{\mathrm{rec}} = (1.8\pm0.3)\cdot10^9$ L mol^{-1} s^{-1}. The radical decay kinetics was determined in solutions, which were purged with oxygen (for the acceleration of the absorption decay of the hydrated electron and triplet ^{3}HSA$^-$), and, hence, the section cut in the ordinate (see Fig. 9) corresponds, most likely, to the reaction of HSA• with oxygen. In oxygen-saturated aqueous solutions $[\mathrm{O}_2] \approx 1.25\cdot10^{-3}$ mol L^{-1},[37] which allows one to estimate the rate constant from the value of this section: $k_{\mathrm{O}_2} \approx 2\cdot10^6$ L mol^{-1} s^{-1}. Low rate constants of the reaction with oxygen are characteristic of phenoxy radicals.[36,38]

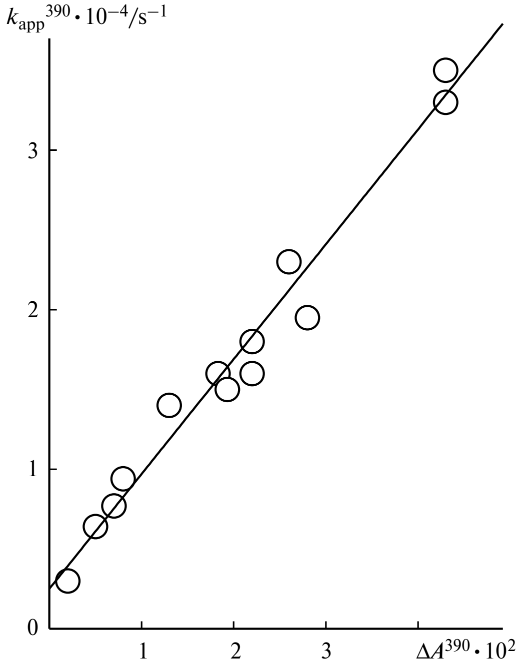

Fig. 9. Dependence of the apparent rate constant of absorption decay of the HSA• radical at 390 nm ($k_{\mathrm{app}}{}^{390}$) on the signal amplitude (ΔA^{390}) at [HSA$^-$]= $2.0\cdot10^{-4}$ mol L^{-1}.

Thus, the band of the triplet-triplet absorption ($\lambda_{\max}$ = 455 nm) of the salicylic acid anion in aqueous solutions was detected by laser flash photolysis. The absorption coefficient of this band was determined using the triplet-triplet energy transfer to 2,2´-dipyridyl. It was shown that at high laser pulse intensities the hydrated electron and HSA• radical are formed. The relaxation rate constants of the excited S$_1$ state and the quantum yields of the triplet state and electron were determined. In a neutral medium, the main decay channels for the triplet state of HSA$^-$, HSA• radical, and hydrated electron are T—T annihilation, recombination, and capture by the anion, respectively. Nanosecond laser flash photolysis of HSA$^-$ in aqueous solutions can be a convenient source of the hydrated electron with a high quantum yield.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 05-03-32474, 06-03-32110, 06-03-90890-Mol, and 05-03-39007GFEN), the Federal Agency on Science and Innovations (State Contract No. 02.444.11.7231), and the Program of Complex Integration Projects of the Siberian Branch of the Russian Academy of Sciences SO RAN-2006 (Grants 4.16 and 77).

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Received January 12, 2007