Photophysics and Photochemistry of 2-Aminobenzoic Acid Anion in Aqueous Solution

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Nanosecond laser flash photolysis and absorption and fluorescence spectroscopy were used to study photochemical processes of 2-aminobenzoic acid anion (ABA^-) in aqueous solutions. Excitation of this species gives rise to the ABA^- triplet state to the $ABA^•$ radical and to the hydrated electron (e_{aq}^-). The last two species result from two-photon processes. In a neutral medium, the main decay channels of ABA^- triplet state, the $ABA^•$ radical, and e_{aq}^- are T−T annihilation, recombination, and capture by the ABA^- anion, respectively.

1. Introduction

Organic acids ($R-CO_2H$) are a class of compounds abundant in natural water.[1] These acids can form complexes with many transient metals (including Fe(III)) whose photochemistry can contribute substantially to the balance of organic compounds in water.[2−8] It is worth noting that aromatic acids have their own strong absorption bands in the UV range and can be subjected to photochemical transformation under solar radiation in a free noncoordinated state.[2]

Salicylic acid (2-hydroxybenzoic acid, H_2SA) and its derivatives (SAD) are considered to be representatives of the complexing functional groups in humic substances[9] and can serve as model compounds for investigating the photochemical properties of natural acids. Photophysics of SAD is widely investigated because these compounds are the simplest systems for studying excited-state intramolecular proton transfer (ESIPT) in a gas phase and liquids.[10−14] However, the photochemical properties of SAD are poorly characterized. It was not until recently that the spectrum of TTA (triplet−triplet absorption) of SAD in organic solvents recorded by laser flash photolysis was published.[11] In our previous works,[15−17] the photochemistry of H_2SA and 5-sulfosalicylic acid (H_3SSA) in aqueous solutions was studied. In a wide pH range, monoanion HSA^- and dianion $HSSA^{2-}$ were found to be the main photoactive forms of H_2SA and H_3SSA, accordingly. Excitation of these species (308 nm, XeCl laser) gives rise to the triplet state, to the hydrated electron, and to the corresponding phenoxyl radical. The last two species result from two-photon processes.[15−17]

In the present work, the photochemical and photophysical processes have been studied for 2-aminobenzoic acid anion (ABA^-) in aqueous solutions in the framework of the program for studying photochemical transformations of organic compounds in natural water. This species is the main photoactive form of the acid at pH values that are typical for natural waters. The main attention was concentrated on the determination of the spectral and kinetic characteristics of primary intermediate states and species formed upon the excitation of ABA^- and comparison of the photochemical properties of anions of 2-aminobenzoic and salicylic acid.

2. Experimental Details

Laser flash photolysis experiments were performed using a setup with a YAG laser excitation (355 nm, pulse duration 6 ns, irradiation spot 0.03 cm^2, mean energy up to 10 mJ/pulse) analogous to that described elsewhere.[16] The laser pulse power was measured using a SOLO-2 “Gentec” power meter.

Nanosecond fluorescence dynamics was measured using the time-correlated single photon counting (TCSPC) setup described elsewhere.[18] Excitation was performed using a diode laser PLC-340 (LDH series, PicoQuant GmbH) at 350 nm and 40 MHz. The data were analyzed using the convolution of the instrument response function with the exponential function. The overall time resolution was ca. 300 ps.

The steady-state fluorescence spectra were measured in a 1 cm cell with a Varian CARY Eclipse spectrofluorimeter. We determined the fluorescence quantum yields by integrating the corrected emission spectra[19] and using a solution of quinine bisulfate in 1 M H_2SO_4 ($\phi = 0.546$) as standard.[20] The absorption spectra were recorded using an Agilent 8453 spectrophotometer.

2-Aminobenzoic acid (HABA, 98%, Aldrich) was recrystallized from aqueous solution before use. The solutions were prepared using bidistilled or deionized water. Unless otherwise specified, all experiments were carried out with oxygen-free samples in a 1 cm optical cell at 298 K. We removed oxygen by bubbling solutions with gaseous argon. Samples for flash photolysis were used until the 10% decrease in UV absorption.

3. Results and Discussion

3.1. Absorption and Fluorescence Spectra of ABA. Depending on the pH, the 2-aminobenzoic acid can exist in cationic (protonation of the amino group, $pK_a(NH_3^+) = 2.1$[21]), neutral, and anionic (dissociation of carboxylic group, $pK_a(COOH) = 4.95$[21]) forms. At circumneutral pH, which is typical for natural waters, the main form of the acid is anion ABA^-. The absorption and emission spectra of this species in aqueous solutions are depicted in Figure 1a. ABA^- exhibits a long-wave absorption band with a maximum at 310 nm ($\varepsilon \approx 2.8 \times 10^3$ M^{-1} cm^{-1}) corresponding to $\pi-\pi^*$ transition,[22] which is typical behavior of SAD.[14] Large Stokes shift of ABA^- fluorescence (~6900 cm^{-1}) is observed indicating that the geometry of the emissive excited state of ABA^- differs significantly from that of the ground state due to ESIPT process. This observation is in

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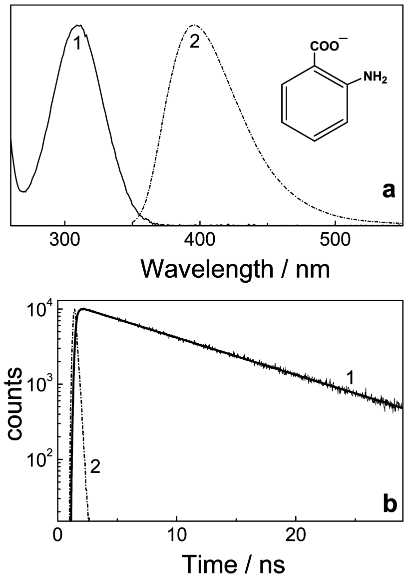

Figure 1. (a) Normalized (1) absorption and (2) fluorescence spectrum of ABA^- in aqueous solution at pH 8. (b) Kinetic curve of (1) ABA^- fluorescence at 400 nm and (2) the instrument response function. Smooth line is the best exponential fit after reconvolution with the instrument response function.

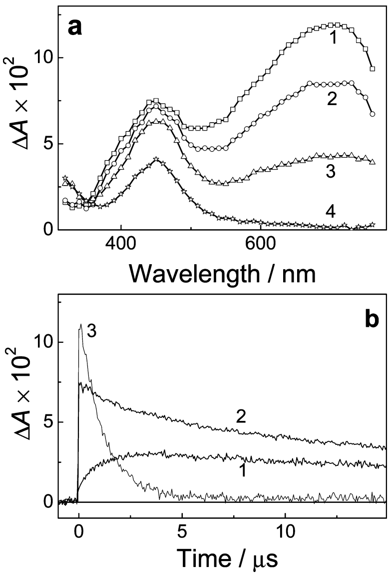

Figure 2. (a) Transient absorption spectra at (1) 0, (2) 0.4, (3) 1.2, and (4) 10 μs after excitation of ABA^- (4×10^{-4} M, pH 8) in oxygen-free aqueous solution. (b) Kinetic curves at (1) 330, (2) 450, and (3) 720 nm.

agreement with previous photophysical investigations on the neutral and anionic forms of SAD in nonpolar[11−13] and polar[13,14] solvents.

The fluorescence quantum yield of ABA^- is $\varphi_{fl} = 0.64$, which makes it possible to determine the rate constant of the radiative process from the S_1 state ($k_{fl} = \phi_{fl}/\tau_{fl} = 7.3 \times 10^7\ s^{-1}$) based on the measured fluorescence lifetime of the anion ($\tau_{fl} = 8.75$ ns, Figure 1b).

3.2. Laser Flash Photolysis of ABA^- Aqueous Solution. Excitation of the oxygen-free aqueous solutions of ABA^- by a laser pulse gives rise to intermediate absorption consisting of two bands with maxima at 450 and 720 nm (Figure 2a). The bands at 450 and 720 nm decay at substantially different rates (Figure 2b), which indicates the formation of several intermediate species after the laser pulse. The band lifetime at 450 nm decreases sharply in the presence of oxygen, which is evidence of the band belonging to ABA^- absorption from the triplet (T_1) state. It worth to note that TTA band of the anionic forms of salicylic and 5-sulfosalicylic acids in aqueous solution has a maximum at 455 and 470 nm, accordingly.[15,17] On the basis of data from pulse radiolysis, it is known that a wide band with a maximum at 720 nm belongs to the absorption of hydrated electron (e_{aq}^-, $\varepsilon^{720} = 2.27 \times 10^4\ M^{-1}\ cm^{-1}$).[23]

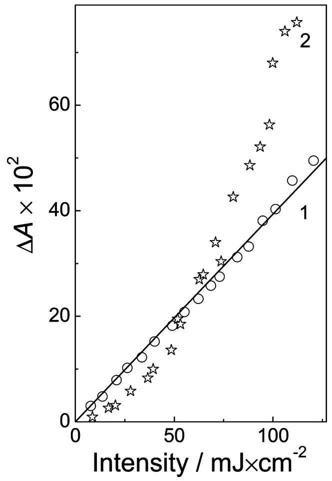

Figure 3. Dependence of the optical density of ABA^- TTA (450 nm) and e_{aq}^- absorption (720 nm) on laser pulse intensity. $[ABA^-] = 1.1 \times 10^{-3}$ M, pH = 8.

Figure 3 presents the dependence of the yield of the TTA of ABA^- and e_{aq}^- on laser pulse intensity. The TTA (450 nm) yield increases linearly, allowing one to determine the product $\varphi(T_1) \times \varepsilon_T^{450} = 3.5 \times 10^3\ M^{-1}\ cm^{-1}$, where ε_T^{450} is the extinction coefficient of the TTA band with a maximum at 450 nm (Figure 2a). The e_{aq}^- absorption yield (720 nm) depends on the laser pulse intensity according to the square law (Figure 3). This indicates a two-photon process of hydrated electron formation.

In the oxygen-saturated aqueous solutions, e_{aq}^- and the triplet state decay rapidly with the characteristic times <50 and ~160 ns, respectively. These conditions make it possible to detect one more long-lived intermediate, whose absorption spectrum consists of absorption band with maximum at 405 nm (Figure 4a). The decay kinetics of this intermediate are presented in Figure 4b. The absorption amplitude at 405 nm (ΔA^{405}) 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}) (Figure 5). These data indicate that the long-lived intermediate is generated in the two-photon process together with the electron.

In our previous works,[15,16] when studying the photochemistry of the sulfosalicylic acid dianion, we have shown that the two-photon ionization of $HSSA^{2-}$ occurs because of 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 2-aminobenzoic acid anion, photoionization occurs from the S_1 state of ABA^- to form the hydrated electron and 2-carboxyanilinyl radical ($ABA^\bullet$). It is worth noting that anilinyl-type radicals have an absorption maximum at 400−420 nm.[24,25] The linear dependence of ΔA^{405} on ΔA^{720} (Figure 5) allows one from the known absorption coefficient of the hydrated electron to determine a similar parameter for the $ABA^\bullet$ radical ($\varepsilon^{405} = 2.6 \times 10^3\ M^{-1}\ cm^{-1}$).

The observed quantum yield of e_{aq}^- at a laser pulse intensity of 100 mJ/cm^2 (~0.26) is five times higher than the corre-

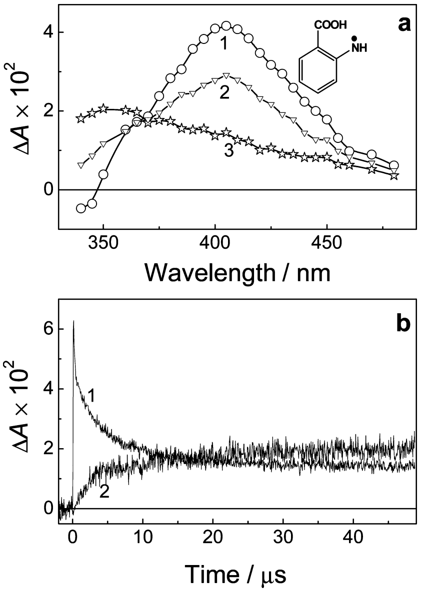

Figure 4. (a) Transient absorption spectra at (1) 0.8; (2) 3.2, and (3) 48 μs after excitation of ABA^- (1.1×10^{-3} M, pH 8) in oxygen-saturated aqueous solution. (b) Kinetic curves at (1) 405 and (2) 350 nm.

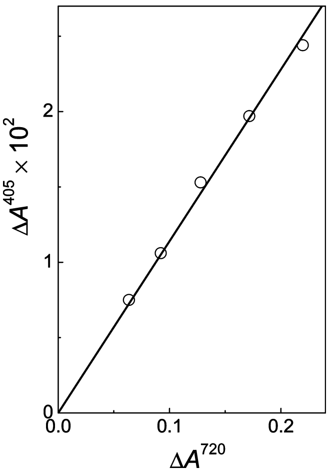

Figure 5. Dependence of the initial absorbance of $ABA^\bullet$ radical (ΔA^{405}) on the initial absorbance of the hydrated electron (ΔA^{720}). $[ABA^-] = 4 \times 10^{-4}$ M, pH 8.

sponding value for the $HSASA^-$ anion (~0.06).[17] This fact could be explained by the following reasons: (1) Ionization potentials of aromatic amines are less than corresponding values for phenols.[26] (2) The lifetime of the S_1 state of ABA^- is two times longer than the one of HSA^- (4.3 ns[13]), which leads to a higher probability of absorbing second light quantum.

3.3. Absorption Coefficient of the Triplet State of ABA. In our previous works,[15,17] the triplet−triplet energy transfer method was used to determine the absorption coefficient from the triplet states of HSA^- ($E_T = 25\,800$ cm^{-1} [27]) and $HSSA^{2-}$ ($E_T = 26\,100$ cm^{-1} [27]). In both cases, 2,2′-dipyridyl (DP), which has the TTA band with a maximum at 350 nm and absorption coefficient 1.8×10^4 M^{-1} cm^{-1},[28] was used as the energy acceptor ($E_T = 23\,500$ cm^{-1} [29]). In this work, the same acceptor was used because E_T of 2-aminobenzoic acid (25200 cm^{-1} [30]) is close to the corresponding values for HSA^- and $HSSA^{2-}$. The excitation energy was adjusted to <10 mJ/cm² to eliminate the two-photon formation of the hydrated electron.

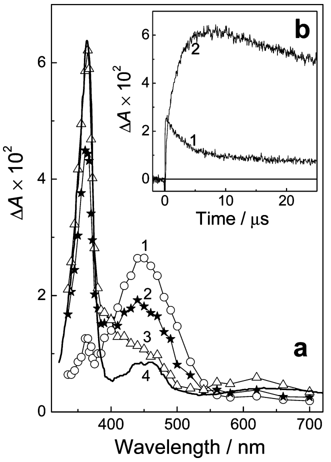

Figure 6. (a) Transient absorption spectra at (1) 0, (2) 2, and (3) 7 μs after excitation of ABA^- (4×10^{-4} M, pH 8) and DP (8×10^{-5} M) in oxygen-free aqueous solution. Curve (4) represents the absorption spectrum of $DPH^\bullet$ radical.[25] (b) Kinetic curves at (1) 450 and (2) 365 nm.

It was observed that in the presence of DP, the TTA band of ABA^- (450 nm) rapidly transforms into two new absorption bands with maxima at 365 and ~620 nm (Figure 6a) belonging to the $DPH^\bullet$ radical ($\varepsilon^{365} = 3 \times 10^4$ M^{-1} cm^{-1})[31] and not to the triplet state of DP. Figure 6b represents the kinetic curves of the absorption change at 450 and 365 nm. Therefore, in contrast with the triplet states of $HSSA^{2-}$ and HSA^-, the reaction of DP with T_1 state of ABA^- leads to the electron transfer and not to the energy transfer

$$^3ABA^- + DP \rightarrow ABA^\bullet + DP^{-\bullet} k_1 \qquad (1)$$

$$DP^{-\bullet} + H^+ \rightarrow DPH^\bullet \qquad (2)$$

The thermodynamic favorability for a given electron transfer reaction may be estimated by the use of the general Rehm−Weller relationship[32]

$$\Delta G^\circ_{ET} = E^\circ(D^+/D) - E^\circ(A/A^-) - \Delta E_{00} - w_p \qquad (3)$$

where $E°(D^+/D)$ is the standard redox potential for oxidation of the donor, $E°(A/A^-)$ is the standard redox potential for reduction of the acceptor, ΔE_{00} is the energy of the excited state for the photoactive component, and w_p is the Coulombic work term. The last three terms are the same in the case of ABA^- and HSA^-. The only difference is the $E°(D^+/D)$ value for these species. Unfortunately, exact values of $E°(ABA^\bullet/ABA^-)$ and $E°(HSA^\bullet/HSA^-)$ are unknown (there is only a rough estimate: $E°(HSA^\bullet/HSA^-) < 1.33$ V[33]), and direct determination of $\Delta G_{ET}°$ for both ABA^- and HSA^- is impossible; however, one can estimate the difference of $\Delta G_{ET}°$ in the case of ABA^- and HSA^- if we assume that $E°(ABA^\bullet/ABA^-) - E°(HSA^\bullet/HSA^-) \approx E°(PhNH^\bullet/PhNH_2) - E°(PhO^\bullet/PhOH) = -0.3$ V.[34] Therefore, one can assume that electron transfer should be more favorable in the case of ABA^- anion.

Kinetic curves of $DPH^\bullet$ formation and decay at 365 nm are well fitted by the two-exponential model

$$\Delta A^{365} = -A_1 \times \exp(-k^{365}_{1obs} \times t) + A_2 \times \exp(-k^{365}_{2obs} \times t) \qquad (4)$$

where A_2, $k_{1obs}{}^{365}$, and $k_{2obs}{}^{365}$ with the $DPH^\bullet$ absorption yield at 365 nm and the observed constants of formation and decay of this radical, accordingly. $k_{1obs}{}^{365}$ increases linearly with an increase in the DP concentration (Figure 7a). This allows one to determine the rate constant of electron transfer $k_1 = 5.5 \times 10^9$ M^{-1} s^{-1} that is close to diffusion one. Decay of $DPH^\bullet$ radical

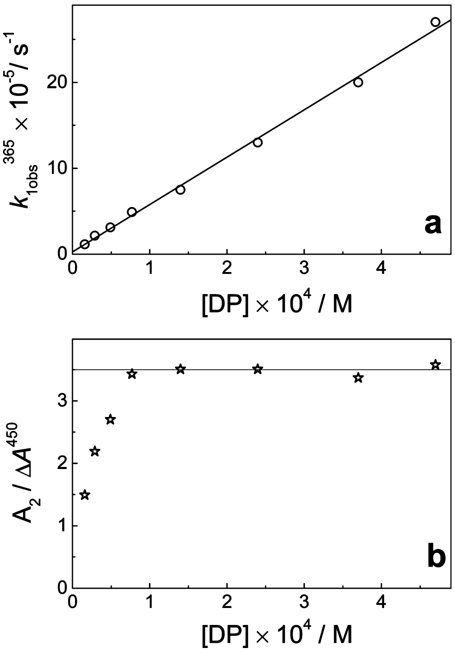

Figure 7. Dependence of the observed rate constant (k_{obs}^{365}) of the DPH$^•$ radical formation (*a*) and the ratio $A_2/\Delta A^{450}$ (*b*) on the initial concentration of DP. [ABA$^-$] = 9 × 10^{-4} M, pH 8.

is determined most probably by reactions with ABA$^•$ and recombination ($2k = 2 \times 10^9$ M^{-1} s^{-1}).[31]

The ratio A_2 to the initial TTA of ABA$^-$ at 450 nm (ΔA^{450}) increases at low concentration of DP and reaches the plateau at concentration of DP > 10^{-4} M corresponding to 100% quenching of triplet state of ABA$^-$ by the acceptor (Figure 7b). In this case, the ratio A_2 to ΔA^{450} is equal to the ratio of the absorption coefficient of DPH$^•$ at 365 nm (ε^{365}) to the T−T absorption coefficient of ABA$^-$ at 450 nm (ε_T^{450}). The calculated value of ε_T^{450} (8.6 × 10^3 M^{-1} cm^{-1}) was found to be close to corresponding values for anionic forms of salicylic and 5-sulfosalicylic acids.[15−17]

The product $\varphi(T_1) \times \varepsilon_T^{450} = 3.5 \times 10^3$ M^{-1} cm^{-1} determined above and the found absorption coefficient allowed one to calculate the quantum yield of the triplet state of ABA$^-$ ($\varphi(T_1)$ = 0.4). The known lifetime of the S_1 state (8.75 ns) and the $\varphi(T_1)$ makes it possible to calculate the intersystem crossing rate constant ($k_{isc} = \varphi(T_1)/\tau_{fl}$ =4.7 × 10^7 s^{-1}). It is worth noting that the sum of quantum yields of the triplet state and fluorescence is close to unity.

3.4. Decay Reactions of e_{aq}^-, T_1 State of ABA$^-$, and ABA$^•$ Radical. ***Hydrated Electron.*** The observed decay rate constant of the hydrated electron (k_{obs}^{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}^- (ΔA^{720}) and the ABA$^-$ concentration (Figure 8a). The intercept on the ordinate by straight lines in Figure 8a depends linearly on the ABA$^-$ concentration and corresponds to electron capture by the anion (Figure 8b)

$$e_{aq}^- + \text{ABA}^- \rightarrow \text{ABA}^{\bullet 2-} \qquad (5)$$

with a rate constant of $k_5 = 1.9 \times 10^9$ M^{-1} s^{-1}, which, with respect to the equal negative charges of reacting species, is close to the diffusion rate constant. Evidence of dianion-radical ABA$^{\bullet 2-}$ formation is the appearance of the transient absorption in the region of 330 nm (Figure 2a,b) with the same time as the lifetime of the hydrated electron. It is worth to note that fast reaction 5 is characteristic for anionic forms of salicylic and 5-sulfosalicylic acids.[15−17] The slope of the straight lines $k_{obs}^{720} \propto \Delta A^{720}$ (Figure 8a) is determined by the second-order reactions

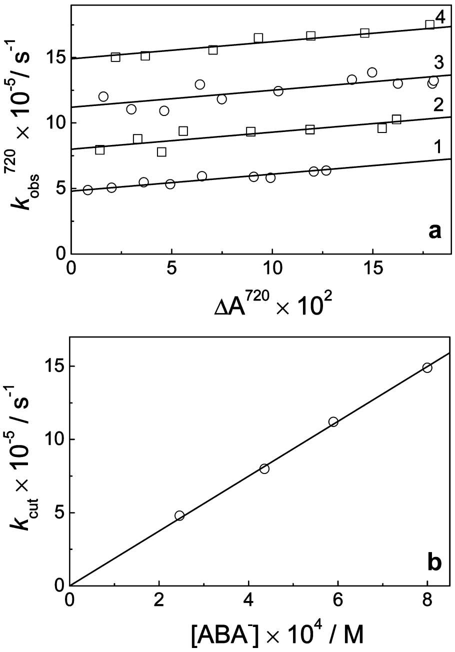

Figure 8. (a) Dependence of the observed rate constant (k_{obs}^{720}) of hydrated electron decay on the initial absorbance at 720 nm (ΔA^{720}) at concentration of [ABA$^-$] × 10^4 = 2.5, 4.4, 5.9, and 8 M, accordingly. (b) Dependence of the intercept in the ordinate by straight lines in part a on ABA$^-$ concentration.

$$e_{aq}^- + e_{aq}^- + 2H_2O \rightarrow H_2 + 2OH^- \qquad (6)$$

$$e_{aq}^- + \text{ABA}^\bullet \rightarrow \text{ABA}^-(S_1) \qquad (7)$$

Processing of the kinetic curves for solutions with different ABA$^-$ concentrations provided the total rate constant $2k_6 + k_7$ = 2.4 × 10^{10} M^{-1} s^{-1}. It is known from experiments on pulse radiolysis of water[35] that $2k_6 = 1.1 \times 10^{10}$ M^{-1} s^{-1}. Therefore, the reaction rate constant for electron capture by the ABA$^•$ radical is $k_7 \approx 1.3 \times 10^{10}$ M^{-1} s^{-1}.

ABA$^-$ Triplet State. The characteristic lifetime of the ^{3}ABA$^-$ in the oxygen-saturated solution ([O$_2$] = 1.25 × 10^{-3} M[36]) is ~160 ns. This lifetime allows one to estimate the constant of triplet state quenching by oxygen, $k_{O2} \approx 5 \times 10^9$ M^{-1} s^{-1}. This value is close to the diffusion limit in water. In oxygen-free solutions, the kinetics of TTA disappearance is substantially determined by the second-order kinetic law. The linear dependence of the observed constant (k_{obs}^{450}) on ΔA^{450} (Figure 9a) indicates that the triplet state mainly decays as a result of T−T annihilation

$$\text{ABA}^-(T_1) + \text{ABA}^-(T_1) \rightarrow {}^1\text{ABA}^-(S_1) + {}^1\text{ABA}^-(S_0) \qquad (8)$$

This reaction results in ABA$^-$ in the excited S_1 state that can convert back into a triplet state. Taking this effect into account, the slope (Δ) of the straight line in Figure 9a can be described by the equation

$$\Delta = 2k_9(1 - \varphi(T_1)/2) \qquad (9)$$

The quantum yield of the triplet state $\varphi(T_1)$ has been determined above. Therefore, the data in Figure 9a can be used to calculate the constant $2k_9 = 10^{10}$ M^{-1} s^{-1}. The intercept on

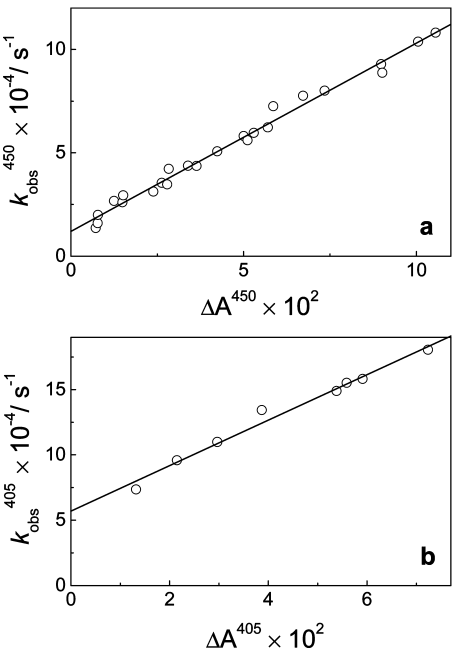

Figure 9. (a) Dependence of the observed rate constant (k_{obs}^{450}) of TTA decay on the initial absorbance at 450 nm (ΔA^{450}). (b) Dependence of the observed rate constant (k_{obs}^{405}) of ABA$^\bullet$ decay on the initial absorbance at 405 nm (ΔA^{405}). [ABA$^-$] = 1.1 × 10^{-3} M, pH 8.

the ordinate ($k_{cut} \approx 10^4$ s^{-1}) corresponds to triplet quenching by residual oxygen (≤2 × 10^{-6} M).

ABA$^\bullet$ Radical. The observed rate constant of ABA$^\bullet$ radical decay (k_{obs}^{405}) in oxygen-saturated aqueous solution depends linearly on the absorption amplitude at 405 nm (Figure 9b). This fact indicates that this species decays in the recombination reaction and makes it possible to determine the corresponding rate constant $2k_{rec} = 4.4 \times 10^9$ M^{-1} s^{-1}. The intercept on the ordinate in Figure 9b corresponds to the reaction of ABA$^\bullet$ with dissolved oxygen ($k_{O2} \approx 5 \times 10^7$ M^{-1} s^{-1}). It is worth noting that the rate constants of reaction of phenoxyl radicals with oxygen are more than one order of magnitude smaller,[16,17] which denotes higher reactivity of anilinyl-type radicals with respect to oxygen.

In oxygen-saturated solutions, the transient absorbance tends to a constant value at ~50 μs after excitation, which indicates the formation of the long-lived transient species (e.g., peroxide radical ABA(O$_2$)$^\bullet$) or the stable photoproducts of reactions of the ABA$^\bullet$ radicals. This conclusion is supported by both the transformation of transient absorption spectrum at $t > 30$ μs (Figure 4, curve 3) and the formation of photochemical products absorbing in the 350−600 nm region (Figure 10). The detailed determination of the nature of final photoproducts will be a subject of further work.

4. Conclusions

The laser flash photolysis was used to record the TTA band (450 nm) of the 2-aminobenzoic acid anion in aqueous solutions. The extinction coefficient of this band was determined using the electron transfer reaction to 2,2′-dipyridyl. At high laser pulse intensities, a hydrated electron and anilinyl ABA$^\bullet$ radical form from two-quantum processes. The rate constants of S$_1$ state relaxation and the quantum yields of the triplet state and the hydrated electron were determined. In a neutral medium, the main decay channels of the triplet state, ABA$^\bullet$ radical, and the hydrated electron are T−T annihilation, recombination, and capture by ABA$^-$, respectively.

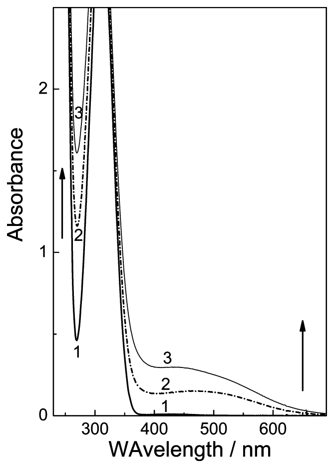

Figure 10. Absorption spectra of air-equilibrated aqueous solutions of ABA$^-$ after (1) 0, (2) 40, and (3) 100 laser pulses with energy 4 mJ/pulse. [ABA$^-$] = 1.1 × 10^{-3} M, pH 8, 1 cm micro cell with volume 0.2 cm^3.

In summary, the photochemical and photophysical properties of 2-aminobenzoic acid anion are analogous to the corresponding properties for anionic forms of salicylic and 5-sulfosalicylic acids. However, ABA$^-$ exhibits higher photochemical activity (i.e., high photoionization and triplet state yields, possible oxidation of ABA$^-$ triplet state by the electron acceptors, high reactivity of ABA$^\bullet$ radical with respect to oxygen). The high yield allows one to use the nanosecond laser flash photolysis of ABA$^-$ in aqueous solutions as a convenient source of a hydrated electron.

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