

# Pulse Radiolysis Studies of Aminobenzenesulfonates: Formation of Cation Radicals

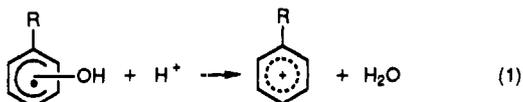
David Behar\*<sup>1</sup> and Bracha Behar<sup>2</sup>

Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556 (Received: December 28, 1990; In Final Form: May 1, 1991)

Sulfanilic acid and anilinedisulfonic acids (ADS) react with OH radicals ( $k = 8.2 \times 10^9$  and  $5.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) to form the corresponding OH adducts. In acid solutions the adducts react with protons to yield cation radicals ( $k = 5.3 \times 10^8$  and  $8.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ).  $\text{N}_3$  oxidizes sulfanilic acid directly to the cation radical by an electron-transfer reaction at a diffusion-controlled rate constant,  $k = 6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , while the rate of oxidation of ADS by  $\text{N}_3$  is only  $7.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ .  $\text{SO}_4^-$  on the other hand oxidizes ADS to the cation radical at a rate of  $1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . Both cation radicals deprotonate to the anilino-type radicals in acid-base equilibria. The  $\text{p}K_a$  of deprotonation of the sulfanilic cation radical is  $5.8 \pm 0.05$  and that of the ADS cation radical is  $4.3 \pm 0.05$ .

## Introduction

Cation radicals have been produced and identified in pulse radiolysis of several aromatic systems where solutes such as methylated benzenes,<sup>3,4</sup> methoxylated benzenes,<sup>5</sup> aromatic amines,<sup>6,7</sup> and aminophenols<sup>8</sup> have been oxidized by  $\text{Ti}^{2+}$ ,  $\text{Ag}_2^+$ ,  $\text{N}_3$ , and  $\text{SO}_4^-$  as well as OH radicals. Cation radicals could not be observed in the oxidation reaction of benzene with  $\text{SO}_4^-$ , although they are most probably formed but are too short lived. Substitution of electron-donating groups on the benzene ring tends to stabilize the cation radicals; therefore, upon addition of methyl groups to benzene rings cation radicals could be observed, the higher the number of methyl groups the higher their stability.<sup>4</sup> All the oxidants mentioned above, excluding OH, react via electron-transfer reactions, while OH radicals add to the benzene ring rather than oxidize it via electron transfer. Therefore, in the reactions of OH with aniline, methoxylated benzenes, or methylated benzenes OH adducts are predominantly formed and only later are transformed by an acid-catalyzed reaction to the cation radical (reaction 1).



The possible formation of cation radicals from alkylbenzenesulfonates has been recently investigated.<sup>9</sup> It was shown that by introducing a sulfonate group to methylated benzenes the transformation reactions of the OH adducts to the cation radicals are completely inhibited. In contrast to the methyl, the sulfonate group withdraws electrons from the ring. When both groups are attached to the same ring, as in the cases of toluenesulfonate or xylenesulfonate, the electron density distribution among the benzene and the substituents is dominated by the electron-withdrawing properties of the sulfonates, leading to electron deficiency on the ring. The net result is that OH adducts decay by a bimolecular process before having any chance to form cation radicals. Direct oxidation of the alkylbenzenesulfonates by  $\text{SO}_4^-$ , which is known to oxidize aromatics by electron-transfer reactions, leads most probably to the formation of positive ion radicals. But these radicals are also too short lived to be observed and undergo rapid conversion to the corresponding OH adduct and benzyl-type radicals.<sup>9</sup> It is therefore interesting to follow the role of cation-radical formation when oxidizing solutes in which the electron-withdrawing sulfonate and a stronger electron-donating group such as  $\text{NH}_2$  are both attached to the same benzene ring. In the present work we looked at the radicals produced in the pulse radiolysis of sulfanilic acid and anilinedisulfonic acid, with a special emphasis on the properties of the cation radicals produced in these systems.

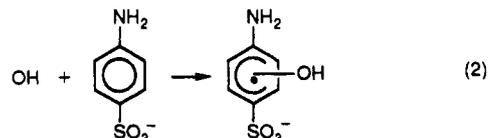
## Experimental Section

Sulfanilic acid from Eastman and aniline-2,5-disulfonic acid (ADS) from Pfaltz and Bauer were recrystallized from water. Sodium azide from Fluka, sodium persulfate from Sigma, mono and disodium phosphate from Baker, and *tert*-butyl alcohol from Fisher were used as received. Solutions were prepared in water purified in a Millipore Milli-Q system. pH was adjusted with  $\text{H}_2\text{SO}_4$  and KOH and with phosphate buffers. For studies of OH reactions, solutions were purged with  $\text{N}_2\text{O}$  prior and during the radiolysis to convert the solvated electrons into OH radicals. When  $\text{SO}_4^-$  radicals were used to react with the solute, 0.2–0.5 M *tert*-butyl alcohol was added to scavenge the OH radicals and the solution was purged with nitrogen.

The spectrophotometric pulse radiolysis setup was described previously.<sup>10</sup> A 7-MeV linear accelerator was used to produce radical concentrations of 2–3  $\mu\text{M}$  per pulse. Dosimetry was performed with  $\text{N}_2\text{O}$ -saturated KSCN solutions taking  $G(\text{SCN})_2^- = 6$  and  $\epsilon(\text{SCN})_2^- = 7600 \text{ M}^{-1} \text{ cm}^{-1}$  at 473 nm.<sup>11</sup>

## Results and Discussion

**(a) Sulfanilic Acid. Reactions with OH.** Aqueous solutions of sulfanilic acid (1–2 mM), at the pH range of 3–10, saturated with  $\text{N}_2\text{O}$  were pulse irradiated and the absorption spectra were recorded. Under these conditions  $\sim 90\%$  of the primary radicals of the water radiolysis are in the form of OH radicals, which in the presence of the solute add to the benzene ring to form hydroxycyclohexadienyl-type radicals (reaction 2). In acid solutions



the OH adduct subsequently undergoes dehydroxylation to form the cation radical (reaction 3). The spectrum obtained at pH

(1) On leave of absence from Soreq Nuclear Research Center, Yavne 70600, Israel.

(2) On leave of absence from the Hebrew University, Jerusalem, Israel.

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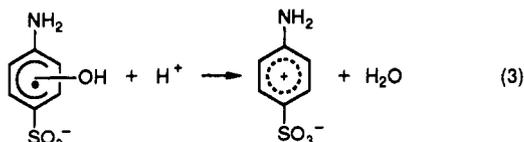
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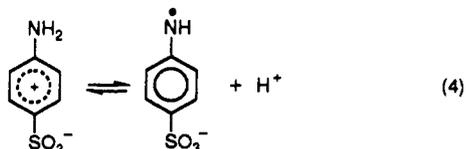
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\* Permanent address: Soreq Nuclear Research Center, Yavne 70600, Israel.



3.3 0.2  $\mu\text{s}$  after the pulse (squares in Figure 1) is interpreted in terms of a mixture of the OH adduct and the cation radical. Since reaction 3 predominates at this pH, the OH adducts rapidly react with the protons and the spectrum observed 8  $\mu\text{s}$  after the pulse is of the cation radical only (circles in Figure 1). A pure spectrum of the OH adduct could be obtained in slightly alkaline solutions where reaction 3 is inhibited. The spectrum of the OH adduct observed after pulse irradiation of a  $\text{N}_2\text{O}$ -saturated solution of sulfanilic acid at pH 10 is given in Figure 2. It is evident that the OH adduct does not absorb at 285 nm and the peak observed at this wavelength at pH 3.3 (Figure 1) originates from the cation radicals present in the acid solutions. From formation curves at 385 nm and at pH 10, a rate of  $8.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was determined for reaction 2. Phillips et al.<sup>12</sup> published a rate of  $2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for the formation of the OH adduct. Their rate constant was derived from absorption curves followed at 270 nm and pH 7. Since the OH adduct has no significant absorption at 270 nm (squares in Figure 2), it is likely that the kinetics observed by them involved the consecutive transformation reaction of the OH adduct to the cation radical. This reaction is pH dependent and as will be shown later catalyzed by phosphate ions. In alkaline solutions the OH adduct decays in a bimolecular process to a stable product. The extinction coefficient of the OH adduct at 385 nm was determined at pH 10,  $\epsilon_{385} = 4900 \text{ M}^{-1} \text{ cm}^{-1}$ . The extinction coefficients of the cation radical at 285 and 445 nm were determined at pH 3.3;  $\epsilon_{285} = 7400 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{445} = 3800 \text{ M}^{-1} \text{ cm}^{-1}$ . (Extinction coefficients accurate to  $\pm 10\%$ .) The rate of reaction 3 has been determined by following the formation curves at 285 and 445 nm as a function of  $[\text{H}^+]$  in the pH range of 2.8–4.3. Figure 3 represents the plot of the pseudo-first-order rate constant for dehydroxylation vs  $[\text{H}^+]$ . From the slope of the linear plot, a rate constant of  $k_3 = 5.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  is derived. The same value within 5% experimental error was found at 445 nm. The fate of the sulfanilic cation radical depends on the pH. Below pH 4 the cation decays in a bimolecular process to a stable product. At higher pH's the cation deprotonates to form the anilinosulfonate radical according to the equilibrium given in reaction 4.



**Oxidation by  $\text{N}_3$  Radicals.** Azide ions react with OH radicals with a rate of  $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ <sup>15</sup> to produce the azide radical, which does not absorb significantly above 300 nm. When  $\text{N}_2\text{O}$ -saturated solutions of 10–40 mM  $\text{NaN}_3$  and 1–2 mM sulfanilic acid in the pH region 4–10 were pulse irradiated, at least 93% of the OH radical were scavenged by the azide ions to form the  $\text{N}_3$  radical. The azide radicals thus obtained oxidize the sulfanilic acid in a diffusion-controlled rate to the cation radical (reaction 5).

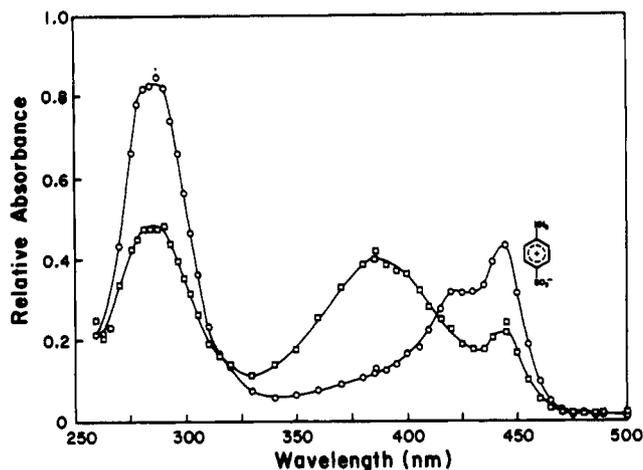
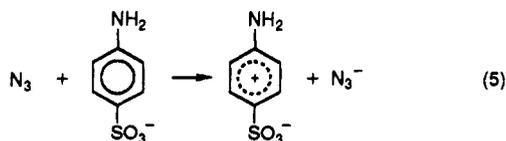


Figure 1. Absorption spectra observed after pulse irradiation of a 1 mM  $\text{N}_2\text{O}$ -saturated sulfonic acid solution at pH 3.3: ( $\square$ ) 0.2  $\mu\text{s}$  and ( $\circ$ ) cation radical 8  $\mu\text{s}$  after the pulse.

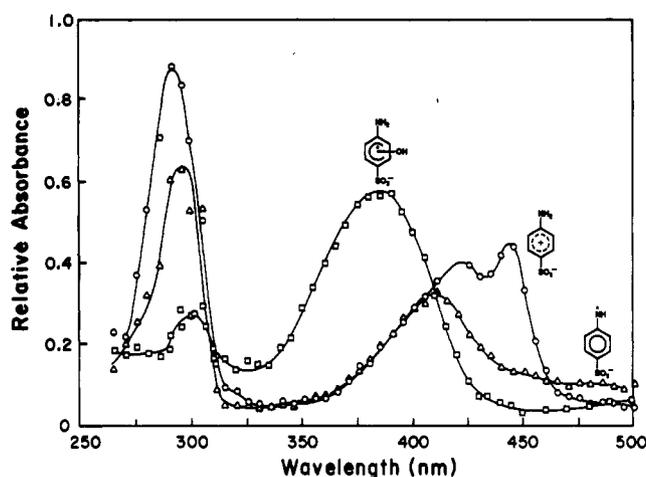


Figure 2. Absorption spectra of ( $\square$ ) OH adduct observed after pulse radiolysis of an  $\text{N}_2\text{O}$ -saturated solution containing 0.5 mM sulfanilic acid at pH 10 and ( $\circ$ ) cation radical and ( $\Delta$ ) anilinosulfonate radical from pulse radiolysis of an  $\text{N}_2\text{O}$ -saturated solution of 1 mM sulfanilic acid and 10 mM  $\text{N}_3^-$  at pH 10, 0.4 and 3  $\mu\text{s}$  after the pulse, respectively.

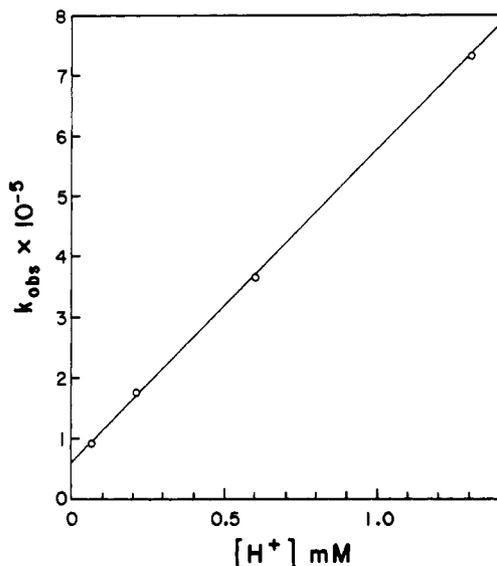
A rate constant of  $k_5 = 6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was determined from absorption increases at 445 nm at pH 7.5. This rate constant is comparable to  $4.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for the oxidation of aniline by  $\text{N}_3^-$ .<sup>7</sup> In alkaline solutions reaction 4 is shifted to the right; therefore, when sulfanilic acid is oxidized with  $\text{N}_3^-$  in alkaline solution, the spectrum of the cation radical is initially observed and subsequently disappears with the concurrent formation of the spectrum of the anilinosulfonate radical. The spectra detected 0.4 ( $\circ$ ) and 3  $\mu\text{s}$  ( $\Delta$ ) after the pulse at pH 10 are given in Figure 2. The spectrum measured 0.4  $\mu\text{s}$  after the pulse contains mainly absorption of the cation radical with some contribution from the anilinosulfonate radical. On the other hand, the anilino-type radical peaking at 410 nm ( $\epsilon_{410} = 1600 \text{ M}^{-1} \text{ cm}^{-1}$ ) is the stable form in alkaline pH; therefore, the spectrum observed 3  $\mu\text{s}$  after the pulse does not contain contributions from any other radicals. As expected the deprotonation of the cation is catalyzed by hydroxyl ions. The pseudo-first-order rate constant of deprotonation as a function of  $[\text{OH}^-]$  was determined by following the absorption at 445 nm in solutions containing  $(1-5) \times 10^{-4} \text{ M OH}^-$ . A rate of  $8.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was determined for the reaction of the cation radical with  $\text{OH}^-$ . This value is somehow lower than  $2.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  found for the parallel reaction of the aniline cation radical with  $\text{OH}^-$ .<sup>7</sup> The deprotonation taking place in reaction 4 was found to be also catalyzed by phosphate ions. A rate constant of  $8.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for the deprotonation reaction by the phosphate was determined at pH 7. It should be mentioned that the oxidation of sulfanilic acid by  $\text{N}_3^-$  at pH < 5.2 is composed

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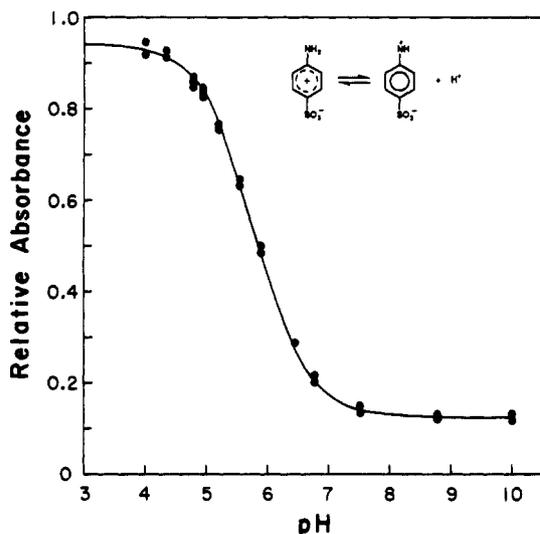
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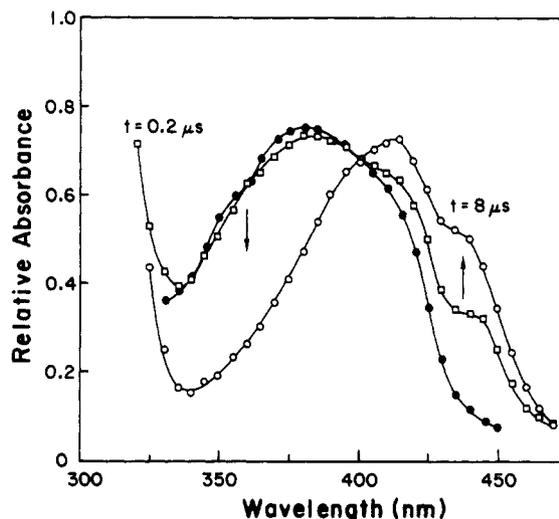
**Figure 3.** Plot of the pseudo-first-order rate of formation at 285 nm of the sulfanilic cation radical from OH adduct as a function of  $[H^+]$ , in the pulse radiolysis of an  $N_2O$ -saturated solution of 0.5 mM sulfanilic acid.



**Figure 4.** pH dependence of the relative absorbance at 445 nm observed 2–6  $\mu s$  after pulse radiolysis of an  $N_2O$ -saturated solution containing 2 mM sulfanilic acid, 40 mM  $NaN_3$ , and 2–4 mM phosphates.

of two distinguishable processes, a fast component, which corresponds to the rate constant of oxidation reported above and relates to more than 80% of the total absorption, and a consecutive component, which is more than 1 order of magnitude slower. A similar behavior has been observed previously in the oxidation of aniline by  $N_3$ .<sup>7</sup> The explanation given there assumed formation of an intermediate that decomposes to  $N_3$  on the longer time scale in an acid-catalyzed process. The mechanism and characterization of such a species is not clear.

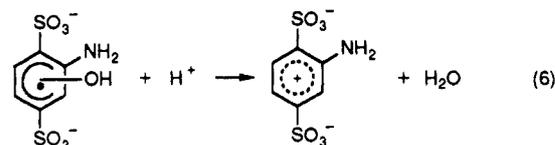
**$pK_a$  of the Sulfanilic Cation Radical.** For the  $pK_a$  determination, the cation radical was produced in solutions containing 40 mM  $NaN_3$ , 2 mM sulfanilic acid, and  $\sim 4$  mM phosphate buffer for pH adjustments in the pH region of 5.5–8. Since the hydrazoic acid has a  $pK_a$  of 4.74,<sup>13</sup> the pH in the region of 4–5.5 was buffered by the azide itself. Absorptions at 445 nm were recorded after the equilibrium between the cation and the anilinosulfonate radicals had been established (5–10  $\mu s$  after the pulse). At the lowest pH studied only  $\sim 16\%$  of the azide is ionized, and since the hydrazoic acid practically does not react with OH radicals,<sup>14</sup>  $\sim 17\%$  of the OH radicals do not react with  $N_3^-$  but with sulfanilic acid to form the OH adduct. Nevertheless, the error in the



**Figure 5.** Absorption spectra observed after pulse radiolysis of an  $N_2O$ -saturated solution of 2 mM anilindisulfonic acid at pH 3.3: ( $\square$ ) 0.2  $\mu s$  and ( $\circ$ ) 8  $\mu s$  after the pulse and ( $\bullet$ ) 1 mM anilindisulfonic acid at pH 10.15 2  $\mu s$  after the pulse.

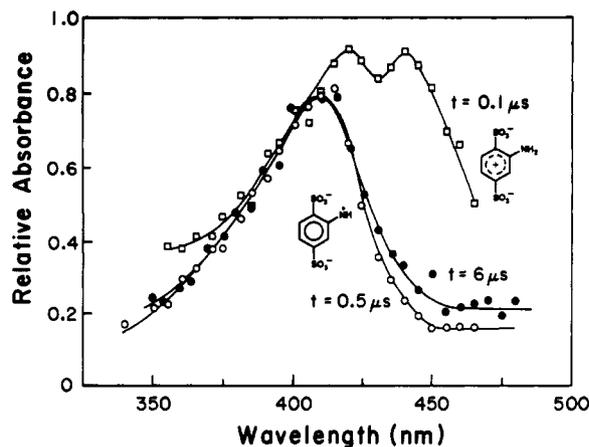
absorption measurement is negligible since at pH 4 most of the OH adducts are transformed to the cation radicals within the time needed for the equilibrium to be established. The experimental results in Figure 4 are best fitted to a calculated curve for a simple acid–base equilibrium having a  $pK_a$  of  $5.8 \pm 0.05$ . A comparison of the  $pK_a$  to other aminobenzene radicals is given below.

**(b) Aniline-2,5-disulfonic Acid. Reactions with OH.** The same sequence of reactions found with sulfanilic acid was found to take place when OH radicals was reacted with ADS. The absorption spectrum obtained in acid solutions immediately after pulse irradiating  $N_2O$ -saturated solution of ADS contains contributions from three different radicals, the OH adduct, the cation radical, and the anilindisulfonate radical (Figure 5). The rate of OH addition was determined by following the absorption buildup at the isosbestic point (400 nm) and at pH 10.15, where the other radicals are not produced. A rate constant of  $5.9 \times 10^9 M^{-1} s^{-1}$  was calculated from pseudo-first-order rate constants obtained at several solute concentrations. This rate compares to  $8.2 \times 10^9 M^{-1} s^{-1}$  found for OH addition to sulfanilic acid. In acid solutions the OH adduct dehydroxylates to form the cation radical. The decay kinetics of the OH adduct at 385 nm is identical with the absorption growth of the cation radical at 440 nm. From the pseudo-first-order growth plots at pH 3.3, a rate constant of  $8.7 \times 10^8 M^{-1} s^{-1}$  was derived for the formation of the cation radical from the OH adduct. The spectrum in Figure 5 at pH 3.3 and



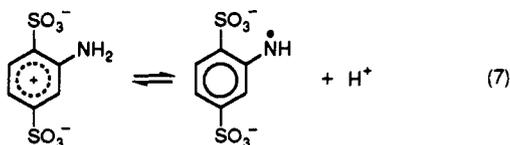
8  $\mu s$  after the pulse (open circles) is composed mainly of the absorption of the cation radical with some contribution from the anilino-type radical, while that obtained at pH 10.15 (full circles) is of the OH adduct. To reveal the contribution of each of the three radicals to the spectrum obtained when ADS is reacted with OH, an indirect approach is needed.

**Oxidation by  $N_3$  and  $SO_4^-$ .** In order to isolate the spectra of the cation and the anilino-type radicals from the OH adduct an attempt was made to oxidize the ADS directly with  $N_3$  and thus avoid formation of the OH adduct. In contrast to sulfanilic acid,  $N_3$  reacts with ADS in a relative very low rate. A rate constant of only  $7.6 \times 10^7 M^{-1} s^{-1}$  was determined for the oxidation by  $N_3$ . This value is 2 orders of magnitude lower than the rate of the parallel oxidation reaction of sulfanilic acid. With such a low rate the formation of the cation radical was always accompanied by a substantial concentration of the anilino-type radical resulting

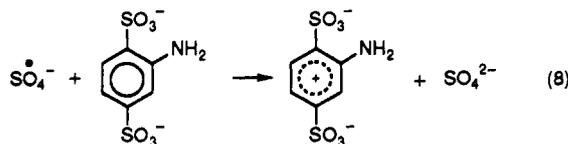


**Figure 6.** Absorption spectra observed after pulse irradiation of an  $N_2$ -saturated solution containing 2 mM anilinedisulfonic acid, 0.1 M  $Na_2S_2O_8$ , 0.5 *tert*-butyl alcohol, and 2 mM phosphate at pH 8: (□) cation radical 0.1  $\mu$ s and (○) anilindisulfonic acid radical 0.5  $\mu$ s after the pulse; (●) anilindisulfonic acid radical from pulse radiolysis of  $N_2O$ -saturated solution of 10 mM ADS, 100 mM  $NaN_3$ , and 5 mM phosphate at pH 7.1 6  $\mu$ s after the pulse.

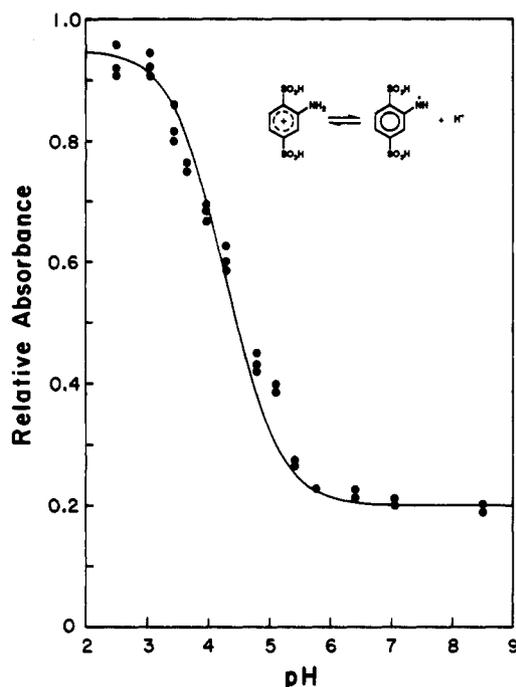
from fast deprotonation (reaction 7) before the oxidation by  $N_3$  has been completed.



Lowering the pH might shift the equilibrium of reaction 7 to the left, but the use of a high  $H^+$  concentration is restricted by the  $pK_a$  of the hydrazoic acid. Therefore, the use of another oxidant was needed, and  $SO_4^{\cdot-}$  was found to be appropriate. Persulfate reacts with hydrated electrons with a rate of  $1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  to produce the  $SO_4^{\cdot-}$  radical,<sup>15</sup> which subsequently oxidizes ADS to the cation radical. In order to avoid any scavenging of electrons



by ADS the concentration of the persulfate was kept at least 20 times greater than the concentration of ADS. OH radicals were scavenged by *tert*-butyl alcohol. The rate of oxidation was determined at pH 2.9 by following after the formation curves at 440 nm and several solute concentrations. From the linear plots of the pseudo-first-order rate constants vs  $[ADS]$ , a rate constant of  $k_8 = 1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  was found. With such a rate constant the spectrum of the cation radical could be isolated immediately after the oxidation reaction had been completed. The spectrum of the ADS cation radical at pH 8 detected 0.1  $\mu$ s after the pulse with slight contribution from the anilino species is given in Figure 6. It has two equally intense absorption maxima at 420 and 440 nm and a strong absorption below 325 nm. The cation radical rapidly deprotonates at this pH so that 0.5  $\mu$ s after the pulse the conversion of the cation to the anilindisulfonate radical is complete (open circles in Figure 6). For comparison the anilino-type radical was also produced by oxidizing ADS with  $N_3$ . Although as mentioned above the pure spectrum of the cation radical could not be isolated when azide was used, the spectrum of the anilino radical could be easily obtained after the deprotonation is complete. The spectrum thus obtained 6  $\mu$ s after the pulse at pH 7.1 fits very well with that obtained from oxidation by  $SO_4^{\cdot-}$ . The spectrum in Figure 6 (full circles) obtained from azide has been normalized at 410 nm to that obtained from persulfate. The



**Figure 7.** pH dependence of the relative absorption at 440 nm observed 3–8  $\mu$ s after pulse irradiation of an  $N_2$ -saturated solution containing 1 mM ADS, 50 mM  $Na_2S_2O_8$ , 0.5 M *tert*-butyl alcohol, and 2 mM phosphates.

extinction coefficient at 410 nm when calculated from the reaction with the sulfate radical by assuming  $G(SO_4^{\cdot-}) = 2.85$  or from the azide radical by assuming  $G(N_3) = 5.4$  gave, in both cases,  $\epsilon_{410} = 1800 \pm 170 \text{ M}^{-1} \text{ cm}^{-1}$ . It should be mentioned that a slow thermal oxidation of ADS by  $S_2O_8^{2-}$  took place during the pulse radiolysis experiment, indicated by the appearance of light purple coloration of the solution.

**$pK_a$  of the ADS Cation Radical.** The cation radical derived from ADS was produced by reacting  $SO_4^{\cdot-}$  radicals with ADS in  $N_2$ -saturated solutions containing 1 mM ADS, 50 mM persulfate, 0.5 M *tert*-butyl alcohol, and 2 mM buffer phosphate. The absorption changes at 440 nm as a function of pH were recorded 3–8  $\mu$ s after the pulse. This was the time required for equilibrium 7 to be established. The results are presented in Figure 7 and are best fitted to a calculated curve of a simple acid–base equilibrium with  $pK_a = 4.30 \pm 0.05$ .

## Conclusions

Cation radicals from sulfanilic acid and anilinedisulfonic acid could be formed either by direct oxidation of the parent molecules with  $N_3$  and  $SO_4^{\cdot-}$  radicals or from the OH adducts. It is evident therefore that the effect of the sulfonate groups to decrease the stability of the cation radicals, by withdrawing electrons from the benzene ring, is overruled by the strong electron-donating nature of the  $NH_2$  group. The  $pK_a$ 's of the cation radicals derived from aniline, sulfanilic acid, and anilinedisulfonic acid, 7.05,<sup>7</sup> 5.8, and 4.3, respectively, show that addition of sulfonate groups to the benzene ring causes a lowering of the  $pK_a$  by 1.25 units for the first addition and 1.5 units for the second sulfonate group added. For comparison, the variations in the  $pK_a$  for protonation of the amine groups in the parent compounds show the same trend. Aniline with  $pK_a = 4.6$ ,<sup>16</sup> sulfanilic acid with  $pK_a = 3.2$ ,<sup>16</sup> and ADS with  $pK_a = 1.7$ <sup>17</sup> exhibit similarly decreases in the  $pK_a$  of 1.3 and 1.5 units upon insertion of the sulfonate groups into the

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(17) The  $pK_a$  of ADS was determined by us by following after the absorption changes of ADS solution at 311 nm as a function of pH and fitting the experimental results to a calculated curve.

ring. It seems that, in both the parent compounds and the cation radicals derived from them, the effect of lowering the  $pK$  by increasing the number of sulfonate groups on the benzene ring is simply an effect of increasing negative charge in the molecule or the radical.

**Acknowledgment.** The research described herein was supported by the office of Basic Energy Sciences of the Department of Energy. This is contribution No. NDRL3372 from Notre Dame Radiation Laboratory. We are grateful to Dr. R. H. Schuler for valuable discussions.

## COMMENTS

### Comment on "Direct Deconvolution of Extensively Perturbed Spectra: The Singlet-Triplet Molecular Eigenstate Spectrum of Pyrazine"

*Str.* High-resolution laser spectroscopy allows the eigenstate-resolved study of intramolecular dynamics, where the dynamics may be intersystem crossing, internal conversion, intramolecular vibrational energy distribution, or isomerization. In these studies one is often in the "intermediate case limit" where transitions to expected isolated states are broken up into small to large numbers of resolved eigenstates due to the dynamics. The basis states that carry absorption strength from a given initial state are known as bright states, and the other basis states are known as dark states. In cases where absorptions from different bright states do not overlap, it is possible to analyze the spectrum in terms of a phenomenological relaxation Hamiltonian for each individual bright state

$$H = e_b|b\rangle\langle b| + \sum_{d=1}^{N-1} e_d|d\rangle\langle d| + f_d(|d\rangle\langle b| + |b\rangle\langle d|) \quad (1)$$

This Hamiltonian has the dark states "pre-diagonalized" and thus has zero coupling between dark states. One is always free to choose such a basis, and since an absorption spectrum is directly sensitive only to the character of the bright state, this is a convenient starting point. This form of the Hamiltonian has been widely used and has been called the "canonical form" by Robinson and Langhoff.<sup>1</sup> If in a spectrum one observes a set of lines to  $N$  eigenstates, then one knows  $N$  eigenenergies ( $\nu_i$ ) and  $N$  intensities ( $I_i$ ). The absolute intensity depends upon the absorption strength of the bright state, and thus only the  $N - 1$  relative intensities are relevant to the dynamics. The relaxation Hamiltonian for one bright state interacting with  $N - 1$  dark states has exactly  $2N - 1$  free parameters, and thus one may in principle invert the problem to determine the  $N$  unperturbed energies and  $N - 1$  coupling matrix elements. It is clear that the solution will be indeterminate as to the sign of the matrix elements, but it was not obvious until recently that a unique solution exists beyond that ambiguity or how to construct any solution.

Berg<sup>2</sup> provided a general solution to this problem, for the case where the dark states can be considered a continuous set  $d(E)$ . She showed how the product  $f_d^2(E) \rho(E)$ , where  $\rho(E)$  is the density of dark states, could be calculated from the matrix element  $G_{bb}(E)$ , where  $G(E)$  is the Green's function.  $\text{Im } G_{bb}(E)$  can be directly calculated from the absorption spectrum, and  $\text{Re } G_{bb}(E)$  can be calculated from  $\text{Im } G_{bb}(E)$  by the Kramers-Kronig integral relation.

Lawrance and Knight<sup>3</sup> (LK) reformulated Berg's procedure and showed how it could be simplified in the case of fully resolved spectra to avoid the calculation of the singular Kramers-Kronig integral. This method is based upon expressing the energy Green's

function  $G(E)$ , in both the eigenvector and initial basis sets. By equating the  $G_{bb}(E)$  matrix element in both basis sets, one gets

$$G_{bb}(E) = \sum_{k=1}^N \frac{I_k'}{\nu_k - E} = \left[ e_b - E - \sum_{d=1}^{N-1} \frac{f_d^2}{e_d - E} \right]^{-1} \quad (2)$$

where the reduced intensities are given by

$$I_k' = I_k / \sum_{j=1}^N I_j$$

This can be rearranged to give

$$\sum_{d=1}^{N-1} \frac{f_d^2}{e_d - E} = e_b - E - \left[ \sum_{k=1}^N \frac{I_k'}{\nu_k - E} \right]^{-1} \quad (3)$$

LK suggested putting in the experimental data ( $I_k'$  and  $\nu_k$ ) with some arbitrary damping width ( $\nu_k$  replaced by  $\nu_k + i\Gamma$ ) and evaluating the right-hand side of eq 3 as a function of  $E$  to find resonances corresponding to each of the  $e_d$ . This is somewhat problematic in that one must use a damping width  $\Gamma$  (and thus a calculated point spacing) much smaller than any of the observed energy level spacings to be sure the individual resonances are nonoverlapping and thus independent. The long tails of Lorentzian lines are particularly troublesome, causing shifts in the calculated peaks on the order of  $\Gamma^2/(e_d - e_d')$ . States with small  $f_d$  will require particularly small  $\Gamma$  not to be lost in the tails of other states since the intensity of the resonance scales as  $f_d^2$ .

We note that the third term on the right-hand side of eq 3 must diverge in order that the left-hand side have a pole at  $E = e_d$ . Thus, the energies of the dark states  $e_d$  are the roots of the function  $h_1(E)$  where in general

$$h_n(E) = \sum_{i=1}^N \frac{I_i'}{(\nu_i - E)^n} \quad (4)$$

This function has poles at each observed eigenvalue  $\nu_i$  and is monotonically increasing in each interval  $[\nu_i, \nu_{i+1}]$ , and thus has one root in each of these  $N - 1$  intervals, and these are the only roots. These roots can be found easily by the method of bisection. Referring to eq 3, it is clear that the residual of the pole at  $e_d$  is just  $f_d^2$ ; thus

$$\frac{1}{f_d^2} = h_2(e_d) = \sum_{i=1}^N \frac{I_i'}{(\nu_i - e_d)^2} \quad (5)$$

The bright state energy can be calculated from the center of gravity of the observed transitions.

$$e_b = \sum_{k=1}^N I_k' \nu_k \quad (6)$$

The root mean coupling matrix element can be evaluated directly from

$$\sum_{d=1}^{N-1} f_d^2 = \sum_{k=1}^N I_k' (\nu_k - e_b)^2 \quad (7)$$

(1) Robinson, G. W.; Langhoff, C. A. *Chem. Phys.* 1974, 5, 1.

(2) Berg, J. O. *Chem. Phys. Lett.* 1976, 41, 547.

(3) Lawrance, W. D.; Knight, A. E. W. *J. Phys. Chem.* 1985, 89, 917.