pair without even transitory formation of a trapped ion-molecule pair. Such "longer range" electron-transfer contributions can account further for the rate-electronic structural demarcations observed here.

Irrespective of the detailed dynamics, then, the present results are considered to provide direct evidence that donor-acceptor electronic coupling as well as nuclear reorganization (i.e.,  $\Delta E^*$ ) can retard the rates of some gas-phase electron-transfer processes. The relative  $k_{ex}$  values for the other metallocenes considered here are also roughly consistent with this interpretation. In particular, the larger gas-phase  $k_{ex}$  value for  $Cp'_2Fe^{+/0}$  versus  $Cp_2Fe^{+/0}$  is in harmony with the corresponding solution-phase rates (Table I), consistent with the expectation that the methyl substituents engender greater donor-acceptor electronic coupling.<sup>3,6b</sup>

The diagnosis of electronic-coupling effects on gas-phase electron-transfer reactivity is probably masked in many cases by uncertainties in the reaction energetics, especially in  $\Delta E^*$ . Even in the present examples, uncertainties in both  $\Delta E^*$  and  $\Delta E_w$  restrict the interpretation to a largely qualitative one. Nevertheless, given that the cusp barrier height  $\Delta E^*_c$  is probably larger for Cp<sub>2</sub>Co<sup>+/0</sup> than for  $Cp_2Fe^{+/0}$  (vide supra), there seems little doubt that the faster kinetics observed for the former couple are due to electronic coupling factors. These may influence  $k_{ex}$  perhaps by decreasing  $\Delta E^*$  and by increasing  $\Delta E_w$  as well as by enhancing the reaction adiabaticity within the encounter complex.

Other documented examples of electronic coupling effects in gas-phase electron transfer are hard to find. A recent study of gas-phase electron transfer between substituted nitrobenzene molecule-radical anion pairs suggests that electronic coupling plays a role in the observed rate variations.<sup>23</sup> Richardson et al. have reported a very small  $k_{ex}/k_{cap}$  value, 0.03, for Ru(hfac)<sub>3</sub><sup>0/-</sup> gasphase self-exchange<sup>7b</sup> (hfac = hexafluoroacetylacetonate). A recent analysis indicates that this reaction is impeded by marked nonadiabaticity both in homogeneous solution and at electrode surfaces.<sup>24</sup> The weak electronic coupling for this system is understandable in view of the "insulation" provided by the fluorinated organic ligand. It seems plausible, then, that the small gas-phase reaction efficiency for  $Ru(hfac)_3^{0/-}$  is also due to the presence of substantially nonadiabatic pathways within the encounter complex, especially since  $\Delta E^*$  is likely to be small or moderate.<sup>24</sup>

Even given the complications wrought in the gas-phase processes by the uncertainties in the dynamics and energetics of encounter-complex formation, the further examination of such reactions, especially those characterized previously in solution, with regard to electronic coupling factors would appear to be well worthwhile.

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## Are Positive Ion Radicals Formed in Pulse Radiolysis of Alkylbenzenesulfonates?

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Oxidation of alkylbenzenesulfonates by OH radicals proceeds via two routes: 75-85% of the OH radicals react via addition to the benzene ring, while the rest abstract an H atom from the alkyl group. The relative distribution between the two paths of reaction depends on the nature of the alkyl group. No evidence for the formation of cation radicals from OH adducts was found. H radicals add to the benzene ring to form cyclohexadienyl type radicals, but when reacted with isopropylbenzenesulfonate about 15% of the H radicals abstract hydrogen from the alkyl to form the benzyl type radical. The reaction of SO4<sup>+-</sup> with alkylbenzenesulfonates produces 50-70% OH adducts and the rest are the benzyl type radicals. At high concentrations of solute and persulfate a short-lived precursor to the benzyl radicals has been observed. The precursors observed with p-toluenesulfonate, isopropylbenzenesulfonate, and m-toluenesulfonate decay in a first-order process with the rates 1.4  $\times 10^{6}$ , 9.4  $\times 10^{3}$ , and 2.5  $\times 10^{5}$  s<sup>-1</sup>, respectively. The short-lived precursor is identified as an unstable OH adduct to the benzene ring.

### Introduction

Israel.

Poly(styrenesulfonate), one of the common negatively charged polyelectrolytes, has been used in many photochemical energy storage systems to slow down back reactions of the photochemically produced charged radicals.<sup>1</sup> With such systems, there is the possibility that some of the radicals involved might react with the polyelectrolyte. Recently we found that on reacting poly(styrenesulfonate) with OH radicals, an OH adduct is formed, which subsequently undergoes a unimolecular reaction to yield a positive ion radical that lives for hours.<sup>2</sup> Attempts to demonstrate formation of cation radicals in a monomer model were not conclusive.<sup>2</sup> However, cation radicals have been produced and identified in pulse radiolysis of several aromatic systems in aqueous solutions, where Tl<sup>2+</sup>, Ag<sup>2+</sup>, SO<sub>4</sub><sup>--</sup>, N<sub>3</sub>, and OH radicals have been used

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as the oxidizing species.<sup>3-6</sup> In the present work, possible formation of cation radicals was investigated, using pulse radiolysis as well as in situ ESR flow photolysis for reaction of various radicals with p-toluenesulfonate (p-TS), m-toluenesulfonate (m-TS), p-isopropylbenzenesulfonate (IPBS), and m-xylene-4-sulfonate (XS).

#### **Experimental Section**

p-Toluenesulfonate monohydrate from Aldrich, m-toluenesulfonic acid from Lancaster Synthesis, m-xylene-4-sulfonate from

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Figure 1. Absorption spectra observed 5  $\mu$ s after pulse irradiating 1.5 mM p-toluenesulfonate: (D) OH adduct, pH 3.3, N<sub>2</sub>O; (O) H adduct, pH 1.0, N<sub>2</sub>, 0.2 M t-BuOH; ( $\Delta$ ) p-TS-benzyl radical, pH 13.7, N<sub>2</sub>O.

TCI, sodium persulfate from Sigma, potassium hydroxide and tert-butyl alcohol from Baker, and hydrogen peroxide from Fisher were used as received. Isopropylbenzenesulfonate was synthesized by the method described by Loehnert et al.<sup>7</sup> and Horyns et al.<sup>7</sup> The magnesium salt of IPBS obtained by this method was substituted with potassium by precipitating the magnesium with concentrated KOH solution. Solutions were prepared in water purified in a Millipore Milli Q system. The pH was adjusted with H<sub>2</sub>SO<sub>4</sub> and KOH. When OH reactions were studied, solutions were purged with N<sub>2</sub>O prior to and during the radiolysis to convert the solvated electrons into OH radicals. When H or SO4<sup>-</sup> radicals were reacted with the solute, 0.2-4 M tert-butyl alcohol was added, and the solution was purged with nitrogen.

The spectrophotometric pulse radiolysis setup was described previously.<sup>8</sup> A 7-MeV linear accelerator was used to produce radical concentrations of 1-3  $\mu$ M/pulse. Dosimetry was performed with N<sub>2</sub>O-saturated KSCN solutions taking  $G(SCN)_2^- = 6$  and  $\epsilon((SCN)_2^-) = 7600 \text{ M}^{-1} \text{ cm}^{-1}$  at 473 nm.<sup>9</sup> The in situ ESR photolysis is described elsewhere.<sup>10</sup>

#### **Results and Discussion**

Reactions of Alkylbenzenesulfonates with OH. Aqueous solutions of sulfonates  $(1 \times 10^{-4}-2 \times 10^{-3} \text{ M})$  at the pH range 3-13.7, saturated with N<sub>2</sub>O, were pulse irradiated, and the absorption spectra were recorded. Under these conditions, about 90% of the primary radicals of water radiolysis are in the form of OH radicals, with the rest being in the form of hydrogen atoms. The OH radicals, at pH's below the pK of OH ( $pK = 11.9^{11}$ ), are expected to add to the benzene ring to form cyclohexadienyl type radicals (reaction 1), rather than to abstract hydrogen from the alkyl.



It has been shown that in similar systems containing methylated benzenes, such as toluene, more than 90% of the OH radicals react via addition rather than hydrogen abstraction.<sup>12,13</sup> The addition

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TABLE I: Rates of Reaction (M<sup>-1</sup> s<sup>-1</sup>) of Alkylbenzenesulfonates with OH, O<sup>-</sup>, H and SO<sub>4</sub><sup>--</sup> Radicals in Aqueous Solutions<sup>a</sup>

solute	ОН	OH O <sup>-</sup>		SO₄⊷	
p-TS	6.1 × 10 <sup>9</sup>	9.9 × 10 <sup>8</sup>	1.1 × 10 <sup>9</sup>	$1.5 \times 10^{9}$	
m-TS	7.9 × 10 <sup>9</sup>	1.5 × 10 <sup>9</sup>	2.4 × 10 <sup>9</sup>	1.5 × 10 <sup>9</sup>	
XS	6.8 × 10 <sup>9</sup>	1.0 × 10 <sup>9</sup>	$2.8 \times 10^{9}$	2.9 × 10 <sup>9</sup>	
IPBS	8.0 × 10 <sup>9</sup>	1.2 × 10 <sup>9</sup>	9.6 × 10 <sup>8</sup>	5.4 × 10 <sup>8</sup>	

"Uncertainties in the rate constants are  $\pm 10\%$ .



Figure 2. Absorption spectra observed 2-10  $\mu$ s after pulse irradiating 0.3 mM *m*-toluenesulfonate: (D) OH adduct, pH 3.4, N<sub>2</sub>O; (O) H adduct, pH 1.0, N<sub>2</sub>, 0.2 M t-BuOH; ( $\Delta$ ) m-TS-benzyl radical, pH 13.7, N<sub>2</sub>O.



Figure 3. Absorption spectra observed 4–6  $\mu$ s after pulse irradiating 2.5 mM *m*-xylene-4-sulfonate: ( $\Box$ ) OH adduct, pH 5.9; N<sub>2</sub>O; (O) H adduct, pH 1.0, N<sub>2</sub>, 0.2 M t-BuOH; ( $\Delta$ ) XS-benzyl radical, pH 13.7, N<sub>2</sub>O.



Figure 4. Absorption spectra observed 15  $\mu$ s after pulse irradiating 0.5 mM isopropylbenzenesulfonate: (D) OH adduct, pH 5.0, N<sub>2</sub>O; (O) H adduct, pH 1.0, N<sub>2</sub>, 0.2 M t-BuOH; ( $\Delta$ ) IPBS-benzyl radical, pH 13.7,  $N_2O$ .

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is expected to take place in various sites of the benzene ring. The rate constants for OH addition to the aromatic ring were determined from optical absorption measurements at several solute concentrations. The rates vary from  $6 \times 10^9$  to  $8 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> (see Table I). The rate constant for the OH addition to p-TS is higher by about 65% than a previous determination, where competition kinetics with N,N-dimethyl-p-nitrosoaniline was employed.14

The absorption spectra of the OH adducts to p-TS, m-TS, XS, and IPBS are given in Figures 1a-4a. These broad asymmetrical spectra, with extinction coefficients of 4000-5000 M<sup>-1</sup> cm<sup>-1</sup>, are typical of hydroxycyclohexadienyl type radicals.<sup>13</sup> The spectra of all OH adducts contain some contribution from the corresponding benzyl type radical (see peaks at 260-285 nm in Figures 1a-4a). The benzylsulfonate radicals are formed by direct hydrogen abstraction from the methyl or isopropyl groups (reaction 2). No evidence was found for transformation of OH adducts

$$CH_3C_6H_4SO_3^- + OH \rightarrow CH_2C_6H_4SO_3^- + H_2O \quad (2)$$

to the benzyl type radical, such as observed with methylated benzenes.<sup>13</sup> The relative amounts of the benzyl radicals, measured for p-TS, m-Ts, and XS, are about 15% of the initial OH adduct concentration. In a previous publication by Sehested et al.,<sup>13</sup> it was found that the amount of hydrogen abstraction from methylated benzenes is directly proportional to the number of methyl groups attached to the ring. It was therefore expected that the yield of the benzyl type radical from the reaction of OH with XS would be doubled. Our results with XS and TS do not follow the same trend. In the case of IPBS the amount of the benzyl type radical reaches 25% of the total OH concentration. This higher yield as compared to the other compounds is attributed to the weak C-H bond of the tertiary hydrogen in the isopropyl group.

Reactions of Sulfonates with O. On irradiating N<sub>2</sub>O-saturated solutions at pH 13.7, the OH adduct spectra are not observed any more. Instead intense absorptions at the region of 265-285 nm accompanied by two additional peaks at 300-325 nm are observed (see Figures 1b-4b). Under these conditions, the initially formed hydroxyl radicals are converted to the deprotonated form (O<sup>-</sup>) so that the rate of addition to the benzene ring becomes relatively slow. Rate constants of  $(2-7) \times 10^7$  are typical for O<sup>-</sup> addition to the benzene ring.<sup>15</sup> On the other hand, hydrogen abstraction from the alkyl group by O<sup>-</sup> becomes relatively fast. As a result, formation of benzyl type radicals predominates under the extremely high pH conditions (eq 3). The specific reactivity of  $O^-$ 

$$0^{-} + \bigcup_{SO_{3}^{-}}^{CH_{3}} \longrightarrow \bigcup_{SO_{3}^{-}}^{CH_{2}} + OH^{-} \qquad (3)$$

to produce benzyl type radicals has been observed previously with several aromatic systems.<sup>12,16–19</sup> The spectrum of the benzyl from the *m*-TS isomer is less intense, and the main peak at 258 nm is blue shifted by 7 nm when compared to the benzyl derived from p-TS. In the case of the reaction of  $O^-$  with XS, there is the possibility of hydrogen abstraction from both methyl groups. The position and the narrow shape of the benzyl-XS absorption peak suggest that only one isomer is formed. If a mixture of the pand *m*-benzyl radicals would have been formed, a superposition spectra of the two isomers is expected to yield an asymmetrical

TABLE II: Bimolecular Rate Constants (M<sup>-1</sup> s<sup>-1</sup>) for the Decay of the Radicals from Reactions of H, OH, and O<sup>-</sup> with Alkylbenzenesulfonates<sup>a</sup>

solute	H adduct	OH adduct	benzyl	
p-toluenesulfonate	$1.8 \times 10^{9}$	5.2 × 10 <sup>8</sup>	$2.8 \times 10^{9}$	
m-toluenesulfonate	$1.3 \times 10^{9}$	$2.6 \times 10^{8}$	$8.0 \times 10^{8}$	
m-xylene-4-sulfonate	$7.5 \times 10^{8}$	$1.9 \times 10^{8}$	$5.5 \times 10^8$	
isopropylbenzenesulfonate	1.3 × 10 <sup>9</sup>	$2.3 \times 10^{8}$	1.7 × 10°	

<sup>a</sup> Uncertainties in the rate constants are  $\pm 20\%$ .

broad spectrum. The fact that the maximum absorption of the XS-benzyl radical at 270 nm is closer to the 265-nm peak of the p-TS-benzyl rather than to the 258-nm peak of the m-TS-benzyl favors the identification of the radical site of XS-benzyl on the methyl para to the sulfonate group (reaction 4). Previous findings

$$O^{-} + \bigcup_{\substack{\downarrow \\ SO_3^{-}}}^{CH_3} \longrightarrow \bigcup_{\substack{\downarrow \\ SO_3^{-}}}^{CH_2} CH_3 + OH^{-} \qquad (4)$$

of other benzyl type radicals also show significant differences in the absorption spectra of the meta and para isomers (see, for example, the isomers of nitrobenzyl and cyanobenzyl radicals<sup>19</sup> or the isomers of benzyltoluates.<sup>20</sup> Rates of  $(1-1.5) \times 10^9 \text{ M}^{-1}$ s<sup>-1</sup> were measured for hydrogen abstraction by O<sup>-</sup> (Table I). The rate of the reaction of  $O^-$  with p-TS is about one-half of the rate constant of  $2.1 \times 10^9$  M<sup>-1</sup> s<sup>-1</sup> reported for toluene.<sup>19</sup> This lower rate for p-TS might be partially related to the electrostatic repulsion between the O<sup>-</sup> and the sulfonate.

**Reactions with H Radicals.**  $N_2$ -saturated solutions of 0.3-2.5 mM alkylbenzenesulfonates at pH 1 containing 0.2-0.5 M t-BuOH were pulse radiolyzed. Under these conditions the OH radicals react with the alcohol, producing the  $^{\circ}CH_2(OH)(CH_3)_2$ radical, which is inert toward the sulfonate compounds. The solvated electrons produced during the radiolysis react with the protons to produce H radicals within few nanoseconds. In the presence of sulfonates the hydrogens add to the benzene ring to form a cyclohexadienyl type radical (reaction 5). The rates of

$$H + \bigcup_{SO_3^-}^{CH_3} \longrightarrow \bigcup_{SO_3^-}^{CH_3} H$$
(5)

hydrogen addition are lower by up to a factor of 8 from the rates of OH addition (see Table I). A similar but less pronounced trend was found with methylated benzenes.<sup>13</sup> The absorption spectra of the H adducts are given in Figures 1c-4c. Contrary to all other sulfonates where H reacts only by addition, in the case of IPBS hydrogen abstraction by hydrogen radicals is also feasible (eq 6).



This is attributed to the tertiary hydrogen on the carbon adjacent to the ring, which makes hydrogen abstraction from this position much easier. From the absorptions at 285 nm it is estimated that 15% of the H radicals react via abstraction.

Bimolecular Decay of Radicals. The bimolecular rate constants for the decay of the H adducts, OH adducts, and benzyl type radicals are summarized in Table II. All radicals derived from *p*-TS evidently have the highest rates. The OH adducts as a group are more stable than the H adducts. The same trend was reported

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TABLE III: ESR Parameters for the Radicals Produced in the Reaction of OH and SO4. with p-TS and IPBS<sup>a</sup>

	a <sub>l</sub>	<i>a</i> <sub>2</sub>	a4	<i>a</i> 5	a <sub>alkyl</sub>	g	ref
d t t t t t t t t t t t t t t t t t t t	31.63 (32.5)	8.32 (8.5)	12.70 (13)	2.72 (2.75)	9.33 (3) (9.5)	2.002 51	21
	5.07 (5.25) (5.13)	1.76 (1.75) (1.78)	1.76 (1.75) (1.78)	5.07 (5.25) (5.13)	15.89 (2) (16.25) (16.1)	2.002 65 2.002 54	21 16
	4.59	1.62	1.62	4.59	15.67 (6)	2.002 69	

"Hyperfine constants in gauss accurate to 0.05 G; parameters in parentheses are from refs 16 and 21.



Figure 5. Absorption spectra observed after reacting  $SO_4^{\bullet\bullet}$  with *p*-toluenesulfonate, 10 mM *p*-TS, 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 1 M *t*-BuOH, pH 2.5, N<sub>2</sub>, ( $\Box$ ) 0.1  $\mu$ s and (O) 2  $\mu$ s after the pulse. The insert shows the difference between the observed spectrum at the short time and the normalized spectrum of the benzyl radicals. The factor of the normalization was calculated from the absorption of the benzyl at the wavelengths of maximum absorption.

for the bimolecular decay rates of H and OH adducts of methylated benzenes.<sup>13</sup> There is a moderate effect of the sulfonate charge on slowing down the bimolecular reactions when compared to the bimolecular rates of the radicals derived from methylated benzenes. The greatest effect is found when comparing the bimolecular decay rate of  $1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  for the OH adduct derived from *m*-xylene sulfonate to the rate of  $1.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for the OH adduct derived from *m*-xylene.<sup>13</sup>

ESR of Radicals from p-TS and IPBS. On reacting p-TS with OH by using  $H_2O_2$  as a photolyte in the steady-state ESR flow system, ESR spectra of two radicals accompanied by some unresolved lines have been observed. The radical with the more intense spectrum was identified as the hydroxycyclohexadienyl type radical, with the OH ortho to the methyl group. The second intense spectrum was identified as the p-benzylsulfonate radical. The magnetic parameters of both radicals were previously determined<sup>21</sup> and are in good agreement with the present deter-



Figure 6. Absorption spectra observed after reacting  $SO_4^{--}$  with isopropylbenzenesulfonate, 40 mM IPBS, 0.1 M  $Na_2S_2O_8$ , 4 M *t*-BuOH, pH 2.3,  $N_2$ , ( $\Box$ ) 0.4  $\mu$ s and (O) 4  $\mu$ s after the pulse. The insert shows the same as in Figure 5.

mination (Table III). When  $S_2O_8^{2-}$  is used as photolyte instead of  $H_2O_2$ , the same two radicals are observed but the relative intensities are reversed with the spectrum of the benzyl type radical being the stronger. It should be noted that the relative intensities reflect the steady-state concentration ratio only. Nevertheless in pulsed experiments, the same phenomena of increased benzyl radical concentration was found by changing the oxidant from OH to  $SO_4^{--}$  (see below).

On reaction of IPBS with OH by photolyzing  $H_2O_2$  in the ESR flow system, a large number of weak lines were detected, but the low intensity did not allow their assignment. On the other hand when  $S_2O_8^{2-}$  was used as a photolyte an ESR spectrum of a single radical composed of septet of triplets of triplets was observed. This spectrum is attributed to the benzyl type radical. See Table III for a comparison between the parameters of the benzyl radicals from *p*-TS and IPBS. No evidence of cation radicals formation from the OH adducts or from oxidation by SO<sub>4</sub><sup>--</sup> could be found from the ESR experiments. Also no precursor of the OH adduct formed by the reaction of SO<sub>4</sub><sup>--</sup> with these solutes could be observed.

Reactions of Alkylbenzenesulfonates with  $SO_4^{\bullet-}$  Radicals. Persulfate is known to react with hydrated electrons with a rate of  $1.2 \times 10^{10}$  M<sup>-1</sup> s<sup>-115</sup> to produce the SO<sub>4</sub><sup> $\bullet-$ </sup> radical. The alkylbenzenesulfonates were found to react with hydrated electrons

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Figure 7. Time dependence of relative absorption of radicals observed on pulse irradiation of a solution containing 40 mM IPBS, 100 mM Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and 4 M t-BuOH, pH 3.6, N<sub>2</sub>, ( $\Box$ ) decay of SO<sub>4</sub><sup>--</sup> at 440 nm, (O) decay of precursor at 340 nm, ( $\odot$ ) growth of IPBS-benzyl radical at 285 nm. The solid lines are the best-fit curves.

with rates of  $(1-3) \times 10^9$  M<sup>-1</sup> s<sup>-1</sup>. Therefore, to avoid scavenging of electrons by the sulfonates, the concentration of the persulfate was kept at least 10 times greater than the concentration of the sulfonate. With Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentrations of 0.2 M, the pH could be reduced to 2.4 and still get more than 95% of the hydrated electrons to react with the persulfate rather than with H<sup>+</sup>. OH radicals were scavenged by adding sufficient amount of *tert*-butyl alcohol.

Figures 5 and 6 describe the absorption spectra of the species obtained from the reaction of SO<sub>4</sub><sup>•-</sup> with p-TS and IPBS 0.1 or 0.4  $\mu$ s after the pulse, respectively, and also 2 and 4  $\mu$ s later. The differences between the early and the later spectra (inserts in Figures 5 and 6) indicates in each case the formation of a short-lived species, which is the precursor to the radicals observed later. The absorption time dependences at three regions for the initial reactions taking place with IPBS are shown in Figure 7. It is evident that the decay of the SO<sub>4</sub><sup>--</sup> radical at 440 nm is completed before a significant decay takes place at 340 nm. Half-life periods of 0.20 and 0.73  $\mu$ s have been measured for the two decays respectively (see remarks on the reaction rates of SO4\* with sulfonates later). As seen in Figure 7, the absorption decay at 340 nm is accompanied by a growth of absorption at 285 nm, with exactly the same period. The best-fit curves for the growth and decay reactions gave first-order rate constants of  $9.4 \times 10^5$ and  $9.3 \times 10^5$  s<sup>-1</sup>, respectively. The kinetics at 285 and 340 nm were found to be independent of solute concentration,  $S_2O_8^{2-}$ concentration, and pH in the measured region of 2.4-12.7. It is evident that the species decaying at 340 nm is the precursor of the benzyl radical, which strongly absorbs at 285 nm. Similar kinetic behavior was found with p-TS except that the rate constant for the process is  $1.7 \times 10^6$  s<sup>-1</sup>. When *m*-TS was reacted with SO4<sup>•-</sup>, formation instead of decaying curves were observed at 330-340 nm with a first-order rate constant of  $2.5 \times 10^5$  s<sup>-1</sup> (7-fold slower than the rate found with p-TS). Also here the kinetics of the short-lived precursor was not dependent on the solute concentration and pH. Unfortunately the formation of the m-TSbenzyl radical could not be followed because of strong absorption of the analyzing light below 280 nm. The spectra detected 0.8 and 8  $\mu$ s after the pulse are given in Figure 8.

The lack of any influence of OH<sup>-</sup> on the kinetics of the short-lived species puts an upper limit of  $3 \times 10^7$  s<sup>-1</sup> for the reaction of OH<sup>-</sup> with the precursor from *p*-TS and  $5 \times 10^6$  s<sup>-1</sup> for the precursor from *m*-TS. If the fast-decaying species are assumed to be the corresponding cation radicals, one would expect them to react much more rapidly with OH<sup>-</sup>. Cation radicals are known to react by diffusion-controlled rates with OH<sup>-;5</sup> therefore, this identification is ruled out. Our results are better understood by assuming formation of cation radicals in the first stage (reaction



Figure 8. Absorption spectra observed after reacting SO<sub>4</sub><sup>--</sup> with *m*-TS, solution made of 20 mM *m*-TS, 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 2 M *t*-BuOH pH 2.7, N<sub>2</sub>, (O) 0.8  $\mu$ s and ( $\bullet$ ) 8  $\mu$ s after the pulse.

7), having too short a lifetime to be observed under our experimental conditions.

$$SO_4^{\bullet-} + \bigcirc_{SO_3^{-}}^{CH_3} \longrightarrow \bigcirc_{SO_3^{-}}^{CH_3} + SO_4^{2-}$$
 (7)

Reaction 7 is followed by a rapid reaction with water (reaction 8) to produce several OH adducts at different positions in the

$$\begin{array}{c} \begin{array}{c} \mathsf{C}\mathsf{H}_3\\ \hline \\ \bullet\\ \mathsf{SO}_3^{-}\end{array} + \mathsf{H}_2\mathsf{O} \end{array} \xrightarrow{} \begin{array}{c} \mathsf{C}\mathsf{H}_3\\ \hline \\ \bullet\\ \mathsf{SO}_3^{-}\end{array} - \mathsf{OH} + \begin{array}{c} \mathsf{H}_3\mathsf{C} \\ \bullet\\ \bullet\\ \mathsf{SO}_3^{-}\end{array} + \mathsf{H}^* (8)$$

benzene ring, with the isomer bearing the OH on the carbon adjacent to the alkyl group (ipso-OH adduct) being the most unstable adduct. The fast decay observed at 340 nm is attributed to this isomer, which tends to lose water to form a benzyl type radical. Reaction 9 (and the analogous with IPBS and *m*-TS) is not catalyzed by either H<sup>+</sup> or OH<sup>-</sup>. The proposed mechanism



is in accordance with the finding that all alkylbenzenesulfonates studied yield substantial amounts of OH adducts upon reacting with  $SO_4$ , in the early stages of the reaction. It can be argued that a  $SO_4$  adduct is the precursor rather than the unstable OH adduct. But the similarity of the spectrum of the very short lived species (inserts in Figures 5 and 6) to that of the OH adduct is in favor of the former assignment, although the identification as the ipso- $SO_4$  adduct cannot be completely ruled out.

The absorption growth at 285 nm as demonstrated in Figure 6 shows that most of the benzyl type radical is produced from the unstable precursor rather than by a direct hydrogen abstraction by the  $SO_4^{\bullet-}$ . Because of the limited resolution in time, the possibility of some direct H abstraction by  $SO_4^{\bullet-}$  could not be completely rejected. Another path of reaction that should be considered, at least for some of the compounds studied, is isomerization of the unstable OH adduct to another more stable isomer. Such reactions are difficult to observe because of the similarity of the absorption spectra of the isomers involved. In the case of m-TS, the spectral changes taking place, after the  $SO_4^{\bullet-}$  has reacted with m-TS, suggests that such isomerization does take place (Figure 8). In this system the increase in absorption at the 320-340-nm range could not be attributed to the formation of

m-TS-benzyl radical because of its weak absorption at these wavelengths and is therefore attributed to the isomerization reaction.

Unstable OH adducts were not observed when OH radicals react directly with *p*-TS or IPBS. This is not surprising if we consider the differences in the nature of the reactions involved in the formation of the OH adducts from  $SO_4$ <sup>--</sup> and OH. In the former case the adducts are formed by hydrolysis of the cation radicals, while in the later case a direct OH addition to a double bond takes place.

The reaction rates of  $SO_4^{-}$  with the various sulfonates as given in Table I were determined by following the absorption growth of the OH adducts at 320-340 nm and the decay absorption of SO<sub>4</sub><sup>•-</sup> at 450 nm, at concentrations of 0.2-2 mM. At higher concentrations, the pseudo-first-order rate constants were not linear with the solute concentration when followed at 450 nm. The higher the solute concentration the lower the absolute rate constant. This effect is due to some contribution to the absorbance at 450 nm by the unstable OH adduct. Since the unstable OH adduct absorbs also at 300-340 nm, the correct reaction could be observed in high solute concentrations only at the isosbestic points of the spectra of the OH adducts. The decay of  $SO_4^{*-}$  at 440 nm as given in Figure 7 contains absorption of the ipso-OH adduct, and the absolute rate constant derived from it is misleading. Nevertheless, it was introduced for demonstration purposes only.

### Conclusions

Cation radicals that could be identified as intermediate species

in the transformation of OH adducts of methylated benzenes to the corresponding benzyl radicals<sup>13</sup> were not observable in the reactions of OH with alkylbenzenesulfonates. Furthermore, such transformation does not take place at all with the sulfonates. All benzylsulfonate radicals obtained by reactions of OH originate from direct hydrogen abstraction from the alkyl groups. Upon reacting SO<sub>4</sub><sup>--</sup> with alkylbenzenesulfonates, both the OH adduct and the benzyl type radicals are produced. At high solute and persulfate concentrations, a short-lived precursor to the benzyl radical could be observed. It is assumed that the first step of oxidation by  $SO_4^{-}$  is the formation of cation radicals, which react very rapidly with water to form OH adducts at various positions on the benzene ring. The ipso-OH adduct is the apparent unstable precursor that forms the corresponding benzyl radical by elimination of a water molecule. This ipso-OH adduct is not formed when OH radicals react directly with sulfonates.

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**Registry No.** *p*-TS, 16722-51-3; *m*-TS, 104994-83-4; xS, 85182-92-9; IPBS, 6214-18-2; *p*-TS-benzyl radical, 41876-35-1; *t*PBS-radical, 132751-54-3; OH, 3352-57-6; O<sup>-</sup>, 14337-01-0; H, 12385-13-6; SO<sub>4</sub><sup>--</sup>, 12143-45-2.

# Quenching of Indole Luminescence by Copper Ions: A Distance Dependence Study

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From the decrease in fluorescence and phosphorescence quantum yield in rigid glass matrices it was established that both excited singlet and triplet states of idole compounds are quenched by  $Cu^{2+}$  ions and that the interaction extends over distances that exceed 14 Å. Analyzing time-resolved phosphorescence data in terms of electron-transfer theory, we find that (1) the distance dependence of the rate is well described by an exponential law with an attenuation length of 0.55 Å; (2) electron transfer from the excited triplet state is at least 6 orders of magnitude slower than the maximum theoretical value or the value estimated for the excited singlet state. The quenching ability of copper is maintained also in the reduced state. A comparison of singlet and triplet bimolecular quenching rate constants shows that in fluid solution Cu<sup>+</sup>, relative to Cu<sup>2+</sup>, is an equally good if not a better quencher of indole emission.

## Introduction

The fluorescence and phosphorescence of tryptophan (Trp) residues in proteins provide important intrinsic probes for monitoring both structural and dynamical features of these macromolecules.<sup>1,2</sup> The utility and scope of these spectroscopic methods are often limited by the lack of knowledge of basic photophysical processes. Among them is the nature of the interaction between the excited states of Trp and copper, a metal tightly bound at strategic sites in numerous proteins.

Early studies with Trp and other indole derivatives free in solution demonstrated that  $Cu^{2+}$  quenches its fluorescence at a rate approaching diffusion control.<sup>3</sup> In the bacterial protein azurin, removal of copper or its substitution with inert metals leads to a remarkable increase in fluorescence yield and lifetime.<sup>4-6</sup> The quenching mechanism is unknown. It has been proposed that quenching may be due to energy or electron transfer from Trp

to copper or that it may occur through an enhancement of intersystem crossing by an heavy-atom-type perturbation. In azurin, where the separation between reacting centers is about 10 Å it was even suggested that<sup>6</sup> the effects of copper may be due to its influence on the protonation state of histidine or on the reactivity of methionine, amino acids found in between Trp-48 and Cu.

In this paper, the first of a series of two, we investigate the distance dependence of the quenching interaction between  $Cu^{2+}$  (indirectly  $Cu^+$  as well) and the singlet and triplet excited states of indole. The decrease in fluorescence and phosphorescence

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