

Acid-Base Properties of the Radicals Produced in the Pulse Radiolysis of Aqueous Solutions of Benzoic Acid¹

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Hydrated electrons, produced by pulse radiolysis in aqueous solution, react with benzoic acid ($k = 1.6 \times 10^{10} M^{-1} \text{sec}^{-1}$) and benzoate ($k = 3.2 \times 10^9 M^{-1} \text{sec}^{-1}$) to give transient species with pH-dependent optical absorption spectra. At pH 3.8, $\lambda_{\text{max}} < 290$ ($\epsilon_{\text{max}} > 16,000 M^{-1} \text{cm}^{-1}$) and 420 (1600); at pH 9.1, λ_{max} 310 (25,000) and 435 nm (5200); at pH 13.2, λ_{max} 322 (27,000) and 445 nm (8000). The dependence of the spectra on pH show that the electron adduct transient species have pK_a values of 5.3 and 12.0. An extended Hückel molecular orbital calculation shows that the electron adds to the molecular π system with a large fraction of the electron density localized on the carboxylate carbon. Protonation takes place on the carboxylate oxygen atoms, not on the aromatic ring, producing absorption spectra that are completely different than that observed for the addition of H atoms to benzoic acid (λ_{max} 350 nm, $\epsilon_{\text{max}} < 4200 M^{-1} \text{cm}^{-1}$) forming the cyclohexadienyl radical, $\cdot C_6H_5(H)CO_2H$. The electron adduct can best be represented as a substituted benzyl radical, $C_6H_5\dot{C}(OH)_2$. Electron addition to benzenesulfonate, on the other hand, yields a spectrum which resembles that of a cyclohexadienyl radical (325 nm, $3700 M^{-1} \text{cm}^{-1}$), $\cdot C_6H_5(H)SO_3^-$. Hydroxyl radicals add to the benzoate aromatic ring to yield $\cdot C_6H_5(OH)CO_2H$ (350 nm, $3800 M^{-1} \text{cm}^{-1}$) and $\cdot C_6H_5(OH)CO_2^-$ (330 nm, $3800 M^{-1} \text{cm}^{-1}$) with $pK_a = 4.4$.

Introduction

The radiolysis of water generates e_{aq}^- , OH, and H as the reactive radical species. Depending on the concentrations of various solute scavengers, one or more of these radicals can be selectively removed producing a relatively clean reaction system. Pulse radiolysis techniques enables the detection and characterization of the reaction intermediates to be made in the micro- and submicrosecond region. Benzoic acid ($pK_a = 4.19$), as the archetype aromatic carboxylic acid, has been subjected to a number of pulse radiolytic studies in aqueous solution from which the transient optical absorption spectra have been determined. Sangster³ found that at pH 12.8, the $e_{\text{aq}}^- + C_6H_5CO_2^-$ reaction resulted in an intense narrow absorption band at 322 nm and a much weaker one at 444 nm which was attributed to the cyclohexadienylcarboxylate radical, $\cdot C_6H_5CO_2^-$, proposed to have been formed upon the rapid protonation of the electron adduct to the aromatic ring. His examination of the pH dependence of the absorption did not extend below pH 11 where the spectral characteristics of the transient were apparently unchanged. In the presence of N_2O , where the e_{aq}^- is efficiently converted into OH (O^- at pH 12.8), a broad band was observed at 330 nm which was attributed to the O^- adduct to the ring. A further clarification of the spectra of the OH adduct, the hydroxycyclohexadienylcarboxylate radical, $\cdot C_6H_5(OH)CO_2^-$, was made by Dorfman who showed that $\epsilon_{330} = 3600 \pm 500 M^{-1} \text{cm}^{-1}$ in neutral solution⁴ but that at pH 3,⁵ λ_{max} 347 nm with $\epsilon_{347} = 3600 \pm 500 M^{-1} \text{cm}^{-1}$. Thus, the

spectra of the OH adducts to benzoic acid and benzoate ion show different λ_{max} . At pH 1 in the presence of CD_3OH ,⁵ where e_{aq}^- are converted into H and OH radicals are scavenged by the alcohol, the H adduct to benzoic acid, $\cdot C_6H_5(H)CO_2H$, exhibits λ_{max} 352 nm with $\epsilon_{352} = 3700 \pm 500 M^{-1} \text{cm}^{-1}$.

In this study we directed our attention to the following questions. (1) What is the spectrum of the electron adduct in other than highly alkaline solution? (2) Why are the spectra reported for the presumably protonated electron adduct to benzoate, $\cdot C_6H_5CO_2^-$, and the H adduct to benzoic acid, $\cdot C_6H_5CO_2H$, so strikingly different? (3) Keeping in mind that the pK_a for benzoic acid is 4.19, what are the pK_a values for the radicals produced in the radiolysis of benzoic acid and how do they arise?

Experimental Section

The details involving the Febetron 705 pulsed radiation source, detection systems, dosimetry, and solution handling techniques have been described previously.⁶

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Table I: Spectral Characteristics, Acid-Base Properties, and Decay Rates of the Transients Produced in the Pulse Radiolysis of Benzoic Acid in Aqueous Solution

System	Reacting species	pH	Transient species	pK _a	λ _{max} , nm	ε _{max} , M ⁻¹ cm ⁻¹	Decay rate constants		
							λ monitor, nm	2k, M ⁻¹ sec ⁻¹	k, sec ⁻¹
10mM C ₆ H ₅ CO ₂ H, 1 M <i>tert</i> -butyl alcohol	e _{aq} ⁻	3.8	C ₆ H ₅ Ċ(OH) ₂	5.3	<290 420	>16,000 1,600	304	>8 × 10 ⁸	...
2 mM C ₆ H ₅ CO ₂ ⁻ , 1 M <i>tert</i> -butyl alcohol	e _{aq} ⁻	9.1	C ₆ H ₅ Ċ(OH)O ⁻	12.0	310 435	25,000 5,200	335	~7 × 10 ⁸	...
2mM C ₆ H ₅ CO ₂ ⁻ , 1 M <i>tert</i> -butyl alcohol	e _{aq} ⁻	13.2	C ₆ H ₅ ĊO ₂ ²⁻	...	322 445	27,000 8,000	328 445	~5 × 10 ⁸	4.6 × 10 ²
10 mM C ₆ H ₅ CO ₂ ⁻ , 1 M methanol	e _{aq} ⁻	13.0	C ₆ H ₅ ĊO ₂ ²⁻	320	1.4 × 10 ⁸	...
5 mM C ₆ H ₅ SO ₃ ⁻ , 1 M <i>tert</i> -butyl alcohol	e _{aq} ⁻	9.0	·C ₆ H ₅ (H)SO ₃ ⁻	...	325	3,700
1 mM C ₆ H ₅ CO ₂ H, 25 mM N ₂ O	OH	3.1	·C ₆ H ₅ (OH)CO ₂ H	4.4	350	3,800	350	1.2 × 10 ⁹	...
1 mM C ₆ H ₅ CO ₂ ⁻ , 25 mM N ₂ O	OH	9.0 to 13.0	·C ₆ H ₅ (OH)CO ₂ ⁻	>14	330	3,800	330	4.4 × 10 ⁸	...
2 mM C ₆ H ₅ CO ₂ H, 1 M <i>tert</i> -butyl alcohol	H	1.0	·C ₆ H ₅ (H)CO ₂ H	...	350	<4,200	350	1 × 10 ⁹	...

Analytical reagent grade chemicals were used throughout and solutions were buffered using perchloric acid, potassium hydroxide, sodium tetraborate, and potassium phosphate. Spectral resolution using two high-intensity Bausch and Lomb monochromators was <2 nm. The concentrations of solutes were chosen on the basis of known radical-radical and radical-solute rate constants.⁷ All values of ε and rate constants reported here were determined within ±20% error.

Results

The reaction of e_{aq}⁻ with benzoic acid or benzoate occurred in solutions containing alcohols such that >98% e_{aq}⁻ and <5% OH react with the substrate. Three distinct intermediate spectra as a function of pH were obtained <1 μsec after the pulse and are shown in Figure 1. The pH curves shown in the inserts were found to be identical for both absorption bands corresponding to deprotonation processes with pK_a values of 5.3 and 12.0. In the presence of 25 mM N₂O, only a very weak absorption remained. The decay of these transients followed second-order kinetics initially, becoming mixed or first order after several half-lives. In general, the second-order rate constant, 2k, decreased as pH was increased. A summary of the decay data is given in Table I. Note that when methanol was used in the solution at pH 13, the initial decay rate constant (1.4 × 10⁸ M⁻¹ sec⁻¹) was smaller than that in *tert*-butyl alcohol solutions (~5 × 10⁸ M⁻¹ sec⁻¹).

The addition of 25 mM N₂O to a solution containing 10 mM benzoic acid and 1 M *tert*-butyl alcohol at pH 3.8 caused a diminution of the optical density of the absorption at 300 nm due to the competitive scavenging of the N₂O for e_{aq}⁻. From a measure of such a decrease in OD, a value of the rate constant for the overall reac-

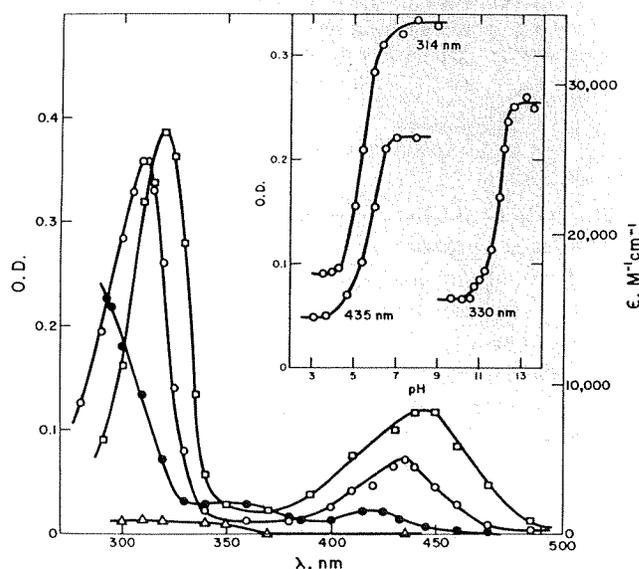


Figure 1. Transient absorption spectra produced in the reaction of e_{aq}⁻ with benzoic acid/benzoate. [Substrate] = 2–10 mM, [*tert*-butyl alcohol] = 1 M, 2.4 krad/pulse. ●, pH 3.8; ○, pH 9.1; □, pH 13.2; △, pH 9.1 in the presence of 25 mM N₂O. Insert: absorption at 314, 330 (2.4 krad/pulse), and 435 nm (8 krad/pulse) as a function of pH.

tion of e_{aq}⁻ with all benzoic acid species was obtained (1.33 × 10¹⁰ M⁻¹ sec⁻¹). From the known value of k(e_{aq}⁻ + C₆H₅CO₂⁻)⁷ and the pK_a of benzoic acid, the rate constant of e_{aq}⁻ + C₆H₅CO₂H was calculated (1.6 × 10¹⁰ M⁻¹ sec⁻¹; see Table II⁸).

Under similar conditions, the transient absorption spectra from the reaction of e_{aq}⁻ with methyl benzoate

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Table II: Second-Order Rate Constants (in units of $M^{-1} \text{sec}^{-1}$) for the Reaction of e_{aq}^- , OH, and H with Benzoic Acid in Aqueous Solution

Solute, S	$k(e_{\text{aq}}^- + S)$	$k(H + S)$	$k(OH + S)$
$C_6H_5CO_2H$	1.6×10^{10}	1.0×10^9 ^a	4.3×10^9 ^b
$C_6H_5CO_2^-$	3.2×10^9 ^c	...	6.0×10^9 ^b

^a Reference 8. ^b Reference 5. ^c Average value at pH 7.4–14 from ref 7.

were examined. In mildly acidic solution λ_{max} for the absorption was <300 nm. In neutral solution, λ_{max} 310 nm with $\epsilon_{310} = 27,000 M^{-1} \text{cm}^{-1}$; a weak absorption at 440 nm was also observed. From the variation of the absorption as a function of pH, a pK_a value of 5.5 was obtained. Results in strongly alkaline solution are meaningless because of the base hydrolysis of the ester.

Completely different results were obtained for $e_{\text{aq}}^- + C_6H_5SO_3^-$. The spectrum of the transient in 1 *M* *tert*-butyl alcohol at pH 9 showed λ_{max} 325 nm with $\epsilon_{325} = 3700 M^{-1} \text{cm}^{-1}$. There was no change in the spectrum even at pH 13.5.

Although the reaction of $OH + C_6H_5CO_2^-$ is fast ($6.0 \times 10^9 M^{-1} \text{sec}^{-1}$),⁵ O^- radicals appear to react more slowly. An apparent rate constant of $8.5 \times 10^7 M^{-1} \text{sec}^{-1}$ was determined at pH 14 from the formation kinetics of the absorption at 330 nm. As Figure 2 shows, the transient spectra of the OH adduct is a function of pH although the spectrum in highly alkaline solution is the same as that of neutral pH. A summary of the spectral and decay characteristics is given in Table I.

The spectrum of the H adduct to benzoic acid, shown in Figure 3, was determined at pH 1 in 1 *M* *tert*-butyl alcohol; the convenience of using such conditions to study H-atom reactions has already been demonstrated.⁹ At $[C_6H_5CO_2H] < 1.5 \text{ mM}$, some H atoms are lost through radical recombination reactions and attack on *tert*-butyl alcohol while at $[C_6H_5CO_2H] > 10 \text{ mM}$, the spectrum of the OH adduct begins to contribute. In the presence of 0.4 *M* 2-propanol, the spectrum of the H adduct disappears due to the preferential scavenging of the H atoms by this alcohol. This latter result demonstrates that any reaction of the *tert*-butyl alcohol radical with benzoic acid (if it indeed takes place) does not contribute towards the spectrum shown in Figure 3. Other H atom scavengers can also be added to benzoic acid at pH 1 in 1 *M* *tert*-butyl alcohol and from the decrease in the OD at 350 nm, provided, of course, that the H-atom transient from the added scavenger does not absorb at that wavelength, relative rates of H-atom attack can be established. For example, using this competitive method; $k(H + \textit{tert}-amyl alcohol) = $3 \times 10^6 M^{-1} \text{sec}^{-1}$ was obtained. It may$

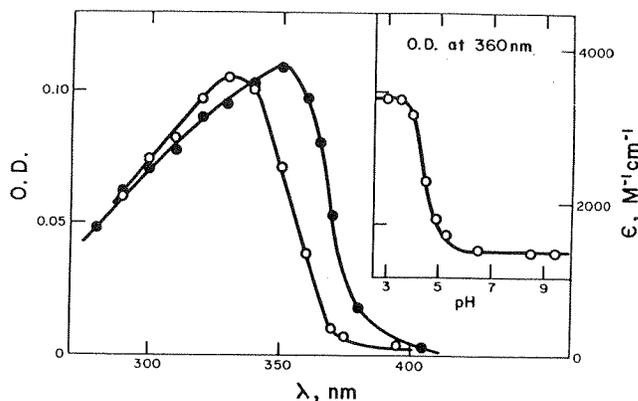


Figure 2. Transient absorption spectra produced in the reaction of OH with benzoic acid/benzoate. [Substrate] = 1 mM, $[N_2O] = 25 \text{ mM}$, 2.4 krads/pulse. ●, pH 3.0; ○, pH 9.3. Insert: absorbance at 360 nm as a function of pH.

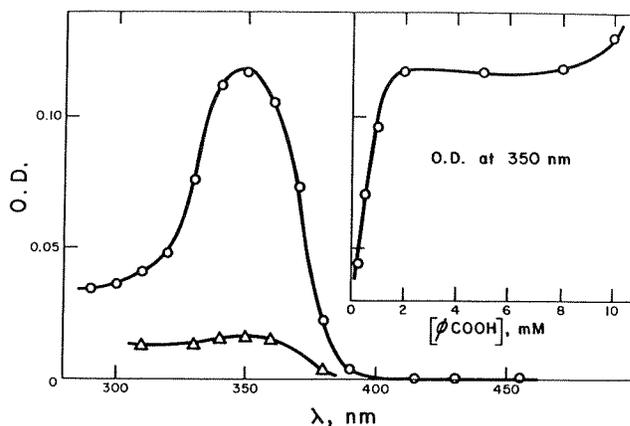


Figure 3. Transient absorption spectrum produced in the reaction of H atoms with 2 mM benzoic acid at pH 1 in the presence of 1 *M* *tert*-butyl alcohol (4 krads/pulse), ○; in the presence of 0.4 *M* 2-propanol, △. Insert: absorbance at 350 nm as a function of [benzoic acid].

be useful to note that $k(OH + \textit{tert}-amyl alcohol), as determined by the CNS^- competitive method,¹⁰ is $1.6 \times 10^9 M^{-1} \text{sec}^{-1}$ making this alcohol a convenient scavenger for both H and OH. The radical produced from the abstraction of an H atom from this alcohol has a weak absorption in the ultraviolet (λ_{max} 225 nm; $\epsilon_{225} = 1100 M^{-1} \text{cm}^{-1}$) which disappears *via* second-order kinetics ($2k = 1.1 \times 10^9 M^{-1} \text{sec}^{-1}$). The spectrum is independent of pH up to pH 14 indicating that this β -hydroxy radical has a $pK_a > 14$.$

Discussion

OH (or O⁻) + Benzoic Acid. The values of λ_{max} , ϵ_{max} , and $2k$ are in very close agreement with those al-

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readily reported⁵ for $\cdot\text{C}_6\text{H}_5(\text{OH})\text{CO}_2\text{H}$ and $\cdot\text{C}_6\text{H}_5(\text{OH})\text{CO}_2^-$, the cyclohexadienyl radicals formed by OH addition to the ring. The observed $\text{p}K_a$ value of 4.4 for the change of spectra as a function of pH is taken to represent the acid-base equilibrium



Thus, the presence of the radical on the ring has little effect on the acidity of the carboxylic acid side chain as compared to the parent acid. In comparison, it should be noted that although the $\text{p}K_a$ of an aliphatic carboxylic acid radical is about the same as the parent acid,¹¹ the $\text{p}K_a$ of an α -carboxy- α -hydroxyalkyl radical appears to be higher than that of the parent, often by more than one $\text{p}K$ unit.¹² This latter effect has been attributed¹² to the delocalization of the unpaired electron by the OH group at the α position so that the inductive effect of the OH group on the dissociation of the acid is reduced.

The radiolysis of benzoic acid yields all three hydroxy derivatives in varying ratios depending on the presence of other scavengers.¹³ Eiben and Fessenden¹⁴ have concluded, on the basis of esr data with benzoate, that the meta and para adducts are produced at the same rate and the ortho at about half the rate per position on the ring. They attribute the lower rate in the ortho position to steric factors. Thus, the broad OH adduct spectrum shown in Figure 2 could be a composite of the overlapping spectra of the three isomers and the observed pH dependence could be a similar composite. Since the $\text{p}K_a$ values for *o*-, *m*-, and *p*-hydroxybenzoic acid are 2.97, 4.06, and 4.48, respectively, it is possible that the observed $\text{p}K_a$ of 4.4 represents an acidity lower or equal to those of the hydroxy acids indicating the reduction of the inductive effect of the OH group. It is not clear from the steady-state radiolysis data whether the state of protonation of the benzoic acid affects the position of attack of the OH radical. It has been proposed,^{13d} in fact, that the OH radical does not attack a specific position on the ring but is rather a complex between the radical and the aromatic electronic system. The specificity of position then arises as a result of the one-electron oxidation step leading to the final, stable products. However, neither pulse nor steady-state radiolysis studies have yet clarified that suggestion.

The second-order decay constants for $\cdot\text{C}_6\text{H}_5(\text{OH})\text{CO}_2\text{H}$ and $\cdot\text{C}_6\text{H}_5(\text{OH})\text{CO}_2^-$ are in agreement with those expected from the Debye relationship¹⁵ for the bimolecular reaction of 0 and -1 charged species in aqueous solution. The independence of the spectrum and decay kinetics on pH between 9 and 13 strongly suggests that the hydroxy group on the radical is not ionized even in highly basic solution. This must be contrasted with the $\text{p}K_a$ of 11.9 for the free OH radical¹⁶ and the acidity constants for the -OH group in the *o*-, *m*-, and *p*-hydroxybenzoic acids of 13.4, 9.9, and 9.3, respectively. However, it must be remembered

that the ring in the $\cdot\text{C}_6\text{H}_5(\text{OH})\text{CO}_2^-$ radical is no longer aromatic and that the hydroxy group is bonded to a tetracoordinated carbon atom forming a secondary alcohol. Thus, the $\text{p}K_a$ for cyclohexanol is >14 ; the $\text{p}K_a$ for the β -, γ -, and δ -hydroxycyclohexyl radicals is expected to be this high, as well.⁶

The reaction of $\text{O}^- + \text{C}_6\text{H}_5\text{CO}_2^-$ is very much slower than that of $\text{OH} + \text{C}_6\text{H}_5\text{CO}_2^-$. The apparent rate constant for the formation of the transient absorption at high pH values consists of a contribution from O^- and OH radicals which are in equilibrium. By taking this equilibrium into account,¹⁷ a value of $k(\text{O}^- + \text{C}_6\text{H}_5\text{CO}_2^-) 4 \times 10^7 \text{ M}^{-1} \text{ sec}^{-1}$ is obtained which is almost an order of magnitude higher than the previously given upper limit obtained indirectly from competition kinetics.¹⁸ This diminished reactivity is attributed to the unfavorable interaction of O^- with the aromatic π system reflecting the diminished electrophilicity of the attacking radical. A similar diminution of the rate has been observed for $\text{O}^- + \text{C}_6\text{H}_5\text{CH}_2\text{CO}_2^-$ (as compared to the OH reaction) although in this case the effect is accompanied by a change in the spectrum of the transient species which reflects transition from OH addition onto the ring to H abstraction by O^- from the methylene group.¹⁷

We have already shown¹⁹ that attack of OH radicals on benzoate coordinated to Co^{III} , in the form of the $(\text{NH}_3)_5\text{CoO}_2\text{CC}_6\text{H}_5^{2+}$ complex, results in OH addition to the aromatic ring with the formation of a transient species that absorbs at λ_{max} 340 nm with a pH-independent spectrum (pH 3-7). The transient decays in a second-order manner with a rate consistent with its charge. These results provide further evidence that the state of protonation or coordination of the carboxylic acid moiety has little effect on the nature of the reaction of OH radicals with the aromatic ring.

H + Benzoic Acid. The details of the spectrum of the $\cdot\text{C}_6\text{H}_5(\text{H})\text{CO}_2\text{H}$ radical likewise correspond well with those reported before.⁵ Furthermore, the similarities between this radical and the OH adducts, similarities that have been noted before between cyclohexadienyl and hydroxycyclohexadienyl radicals in

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general,⁸ strengthens the belief that the H atom adds to a specific position on the ring and that the unpaired electron is similarly localized. Thus, the broad transient spectrum may be the result of the existence of the three substituent isomers, a possibility that an examination of the products of the continuous radiolysis has not yet uncovered. We would predict that the pK_a of $\cdot C_6H_5(H)CO_2H$ would be very similar to that of the parent acid and the $\cdot C_6H_5(OH)CO_2H$ radical.

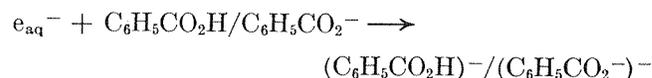
As with the reaction of OH with coordinated benzoate, H atoms at pH 1 react with $(NH_3)_5CoO_2CC_6H_5^{2+}$ to give a transient spectrum with λ_{max} 350 nm which has been identified with addition to the ring.¹⁹

$e_{aq}^- + \text{Benzoic Acid}$. Despite the fact that e_{aq}^- reacts very slowly with benzene ($k = 1.4 \times 10^7 M^{-1} \text{sec}^{-1}$)²⁰ and carboxylate ions such as formate and acetate ($k < 10^6 M^{-1} \text{sec}^{-1}$),²⁰ the reaction of e_{aq}^- with $C_6H_5CO_2^-$ is quite fast, thereby demonstrating the extremely strong interaction between the ring and the carboxylic side chain which provides accessible molecular orbitals for the incoming electron. Protonation of the carboxylate group removes resonance stabilization, increases electrophilicity, and establishes an orbital system with strong carbonylic character thus causing the rate of e_{aq}^- reaction to increase to nearly the diffusion controlled limit. This effect is known for aliphatic carboxylic acids;²⁰ we have demonstrated here that benzoic acid behaves in the same way. It is not clear how these rate constant values can be applied to the Hammett $\rho\sigma$ relationship as given by Anbar and Hart²¹ since the σ_{para} values for $-CO_2H$ and $-CO_2^-$ are 0.45 and 0.0, respectively.²² Perhaps the analogy between the rate of e_{aq}^- reactions and σ values from nucleophilic substitution is questionable, as Anbar and Hart have in fact suggested.²¹

The reduction of benzoic acid by metallic sodium at 77°K generates a species which exhibits an esr spectrum of transient nature;²³ a similar spectrum is obtained from the action of Na in liquid NH_3 on benzoic acid.²⁴ On the basis of these spectra, a conclusion was reached that the transient species was the radical-anion resulting from the addition of an electron to the benzoic acid and could be best represented as a substituted benzyl radical. The product of this reduction in liquid NH_3 in the presence of proton donors such as methanol and ethanol is 1,4-dihydrobenzoic acid.²⁵ This product has not been identified in the radiation chemistry of benzoic acid in aqueous solution.¹³ Presumably its radical precursor from e_{aq}^- addition can undergo secondary reactions, particularly with OH adduct radicals, to yield the hydroxybenzoic acids as the major products. The radiolysis of benzoic acid in the absence of OH radicals has apparently not yet been accomplished.

The reaction of e_{aq}^- and benzoic acid (benzoate) gives three discrete pH-dependent absorption spectra with pK_a values of 5.3 and 12.0. None of the transient ab-

sorptions resembles that of the H adduct at pH 1. The e_{aq}^- would be expected to enter the lowest vacant molecular orbital available which might be considerably delocalized due to the overlap of the π systems of the aromatic ring and the carboxylic side chain. Thus the initial reaction is best described as



An extended Hückel molecular orbital calculation²⁶ shows that the carboxylate carbon in ground state benzoate has a significant partial positive charge while the locus of negative charge is at the oxygen atoms (Table III). The aromatic ring, with its smeared-out electron density, is relatively neutral. Note that protonation of benzoic acid has relatively little effect on the electron charge distribution. It is possible to rationalize the fact that the reactivities of benzoic acid and benzoate with e_{aq}^- are orders of magnitude greater than for benzene in terms of the $\delta+$ contribution of the carboxylate carbon. It is possible that a substantial fraction of the electrons which attack benzoate are initially associated with the carboxylate carbon. The MO calculation also provides insight into the symmetry and distribution of the orbital into which the electron has been promoted. The added electron will be in a π system conjugated throughout the molecule rather than in the σ framework. The greatest contribution to the electron density of the new orbital ($\sim 30\%$) comes from the carboxylate carbon with correspondingly less from the bridgehead carbon and ortho/para positions. The smallest contribution arises from the meta positions indicating that the benzoate radical-anion still remains strongly meta directing towards nucleophilic substitution. The carboxylate oxygens still remain the locus of negative charge in the radical-anion. Because of this negative charge, protonation will take place at the carboxylate moiety. It must be kept in mind that the

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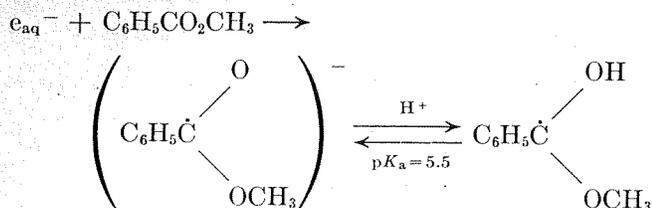
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$e_{aq}^- + Related\ Compounds.$ The spectral and acid-base characteristics of the electron adduct to methyl benzoate are virtually identical with those of the parent acid leading to the conclusion that here too the transient can be represented as a substituted benzyl radical.

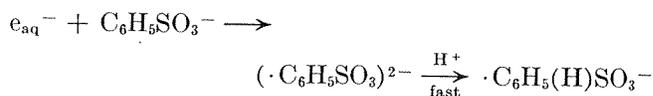


Inasmuch as protonation of benzoate does not have any significant effect on the charges of the atoms other than the carboxylate oxygen (Table III), esterification should likewise have little effect. Thus, in methyl benzoate, the carboxylate carbon would have a significant positive charge and could serve as the site of initial attack by e_{aq}^- . In the case of $(NH_3)_5CoO_2CC_6H_5^{2+}$, where the carboxylate oxygen is bound directly to the Co^{III} metal center, reaction with e_{aq}^- is very rapid ($k = 8 \times 10^{10} M^{-1} sec^{-1}$).³¹ However, it is apparent that the molecular orbital populated provides facile intramolecular electron transfer into the metal center inasmuch as no electron adduct spectrum is observed within the time resolution of the pulse apparatus.¹⁹

The presence of substituents on the benzoic acid ring would be expected to show the effect of variation of orbital interaction between ring and side chain. Thus, the electron adduct to *o*-phthalate at pH 11 has λ_{max} 335 nm with $\epsilon_{335} = 1 \times 10^4 M^{-1} cm^{-1}$. However, in the case of *m*-phthalate in basic solution, λ_{max} 325 nm with $\epsilon_{325} = 1.3 \times 10^4 M^{-1} cm^{-1}$ with a weaker absorption at 450 nm. Evidently the presence of another carboxylate group in the ortho position gives the tran-

sient properties intermediate between that of the cyclohexadienyl radical with the charge localized on the ring and the benzyl type radical with the charge localized on the side chain. With the meta-directing substituents re-enforcing each other, the electron adduct resembles the benzoic acid radical even more.

As Table I shows, the electron adduct to $C_6H_5SO_3^-$ exhibits a spectrum that appears to be characteristic of cyclohexadienyl radicals with λ_{max} 325 nm and $\epsilon_{325} = 3.7 \times 10^3 M^{-1} cm^{-1}$. With no apparent pH dependence of the spectrum up to pH 13.5, we conclude that the vacant orbital into which the electron adds must be strongly localized on the ring; the subsequent rapid protonation of the ring would occur even in alkaline solution.²⁸



It is worth mentioning that the electron adduct to benzene has been searched for unsuccessfully in aqueous solution.³² On the other hand, the electron adduct to biphenyl (λ_{max} 405 nm)²⁸ can be readily seen to decay rapidly by first-order kinetics in aqueous solution even at pH 9 through protonation. The detailed nature of electron addition to aromatic systems, the ultimate in nucleophilic substitution, is still poorly characterized and requires further experimental and theoretical investigations before these details will be known to the same extent as are the rates of e_{aq}^- attack.

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