alignment had been achieved. Good homogeneous alignment was achieved by rubbing plates with cat's fur. Again, the polarizing microscope was used to check alignment.

Acknowledgments. This work was supported in part by a grant from the U. S. Army Research Office—Durham. The Digilab interferometer was purchased under a grant from the National Science Foundation.

Aromatic Hydroxylation Catalyzed by Fenton's Reagent. An Electron Paramagnetic Resonance Study. II. Benzoic Acids

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Unstable free radical intermediates of benzoic acid derivatives (*p*-fluoro-, *p*-chloro-, *p*-bromo-, *p*-hydroxy-, *p*-methoxy-, and *p*-, *m*-, and *o*-nitrobenzoic acids, and 2-, 3-, and 4-pyridinecarboxylic acids) produced by Fenton's reagent (Fe(II) + H_2O_2) were observed by electron paramagnetic resonance, using a continuous flow system. The observed hyperfine structures were analyzed and the molecular structures were assigned on the basis of HMO calculations with the McLachlan modification. All free radicals were the hydroxycyclohexadienyl derivatives, except for a phenoxy radical from *p*-hydroxybenzoic acid. A set of empirical Hückel parameters is introduced for the calculations (*i.e.*, the Coulomb integral for sp^3 carbon is $\alpha + 2.5\beta$, and for its neighboring carbons $\alpha - 0.2\beta$), and the observed hyperfine coupling constants and calculated spin densities agree well with few exceptions. In addition, it is recognized that the attack in hydroxylation occurs at the position(s) possessing minimal localization energy against radical attack and maximal free valence, with few exceptions. The reactive species involved in Fenton's reagent is probably free radical in nature.

Introduction

The reaction mechanism of Fenton's reagent, in particular the nature of the reactive species, has been studied extensively. Electron paramagnetic resonance (epr) studies combined with continuous flow systems certainly have made an epoch in this field. Since the first observation of aliphatic free radicals produced by Fenton's reagent,[1] numerous epr studies have been oriented to the analysis of intermediates[2,3] or to the reaction kinetics,[4-13] comparing them with other oxidation systems (*e.g.*, Ti(III) + H_2O_2).[14] At first sight, Fenton's reagent seemed to be quite different in nature from other oxidation systems, because the observed aliphatic and alicyclic free radicals are dissimilar to those produced by other systems or by the OH radical.[1-3] However, later studies[15-20] have shown that the annihilation of some free radicals by ferric iron must be taken into account for the explanation of our previous results.[1-3] At the same time, we have found that both Fenton's reagent and the Ti(III) + H_2O_2 system produce the same free radicals from furan derivatives.[21] In addition, it is shown that the hydroxylation of furans takes place at the position possessing maximal free valence.[21] On the other hand, some aromatic free radicals produced by the OH radical have been recently reported.[22,23] It is thought that the comparison of the intermediate radicals should be extended to aromatic compounds, therefore, we decided to continue the analysis of the aromatic intermediate free radicals produced by Fenton's reagent.

This paper, thus, primarily concerns itself with the determination of the intermediate free radicals of benzoic acid derivatives produced by Fenton's reagent. In order to assign the observed hyperfine structures to the molecular structures of the hydroxycyclohexadienyl radical, Mc-

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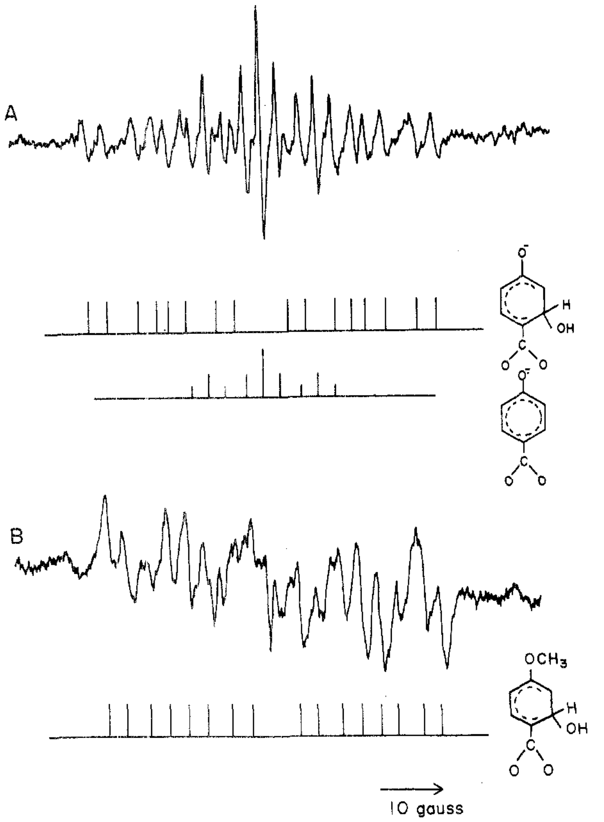

Figure 1. Epr spectra of (A) *p*-hydroxy- and (B) *p*-methoxybenzoic acid radicals. Conditions: (A), modulation 100 kHz, 0.63 G, time constant 0.3 sec, scanning speed 100 G/2 min; and (B), modulation 100 kHz, 1.0 G, time constant 1 sec, scanning speed 100 g/4 min. The arrow at the bottom indicates the direction of the magnetic field strength, and its length corresponds to 10 G.

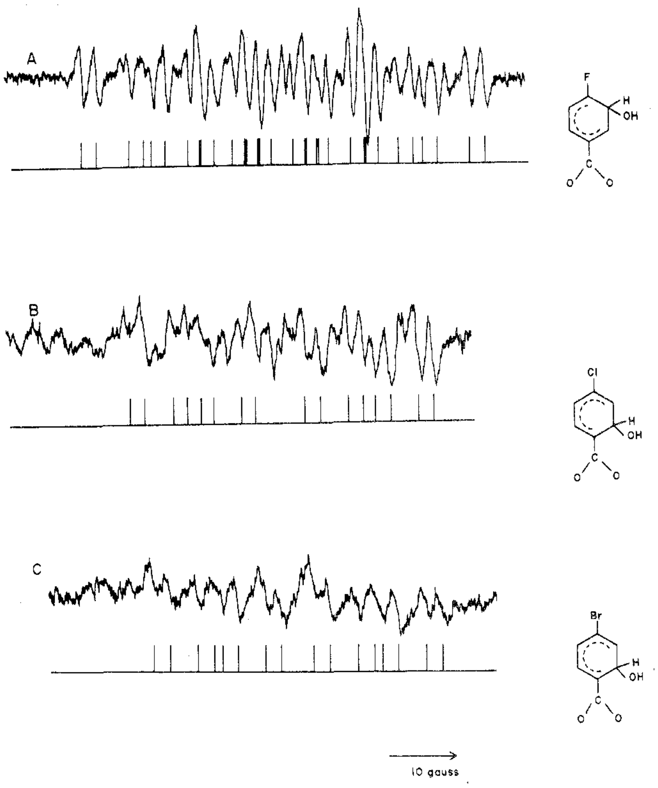

Figure 2. Epr spectra of (A) *p*-fluoro-, (B) *p*-chloro-, and (C) *p*-bromobenzoic acid radicals. Conditions: (A) and (C), modulation 100 kHz, 1.0 G, time constant 0.3 sec, scanning speed 100 G/4 min; and (B), modulation 100 kHz, 0.8 G, time constant 0.3 sec, scanning speed 100 G/4 min. The arrow at the bottom indicates the direction of the magnetic field strength, and its length corresponds to 10 G.

Lachlan calculations were carried out, using a set of empirical Hückel parameters. Finally, the relation between the position of attack and the reactive indices is discussed.

Materials and Methods

Apparatus. A Varian E-12 epr spectrometer was used. The design and characteristics of the continuous flow system have been described previously.[1,24] The pH of the solutions was adjusted by means of a Hitachi F-5 pH meter. All the reagents were of reagent grade and were not purified further.

Methods. The solvent was 0.1 *M* phosphate buffer, pH 7.0. The solution of Fe(II) (5 m*M* of ferrous sulfate)–ethylenediaminetetraacetic acid (5 m*M*) and the solution of H_2O_2 (0.1%) and benzoic acid derivatives (5–10 m*M*, depending on their solubilities) were mixed in the flow cell. Both solutions were bubbled with nitrogen gas in order to remove the dissolved oxygen. The epr spectra were recorded under continuous flow, 7–30 msec after the mixing of the two solutions. The hyperfine coupling constants and g values were measured by comparison with the signal of Fremy's salt, which was sealed in a capillary and inserted beside the flow cell. The g values of the observed free radicals were 2.003. The errors in the coupling constant measurements were within 0.3 G in most cases. The 100-kHz modulation amplitude could not be reduced below 0.25 G, because of poor signal-to-noise ratio. All experiments were carried out at room temperature (23°).

Calculations. A NEAC 2200-500 or a Hitac-10 digital computer was used for theoretical calculations.

Results

Epr Spectra. The epr spectra of *p*-hydroxy- and *p*-methoxybenzoic acid free radicals are shown in Figure 1. The latter spectrum mainly consists of 16 lines of equal intensity, and the former spectrum is composed of two signals: one is 16 lines of equal intensity and the other is 9 lines (with an intensity ratio of 1:2:1:2:4:2:1:2:1). The signals of 16 lines originate from four proton couplings, among which one proton splitting constant is as large as some 30 G, similar to that of the hydroxycyclohexadienyl radical from benzene[22,25] and from benzoic acid.[22] The signal of 9 lines from *p*-hydroxybenzoic acid is the same signal as that of the phenoxy radical reported by Stone and Waters.[26]

The epr spectra of *p*-fluoro-, *p*-chloro-, and *p*-bromobenzoic acid free radicals are shown in Figure 2. The spectra of *p*-Cl and *p*-Br derivatives, again, consist of 16 lines. The spectrum of *p*-fluorobenzoic acid free radical is complicated, but 32 lines can be recognized to which four protons and one fluoride contribute.

The epr spectra of three nitro-substituted free radicals are shown in Figure 3. The spectra of *p*- and *o*-nitroben-

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(24) T. Shiga, A. Boukhors, and P. Douzou, "Recent Development of Magnetic Resonance in Biology," S. Fujiwara and L. H. Piette, Ed., Hirokawa, Tokyo, 1968, p 146.

(25) W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 4857 (1964).

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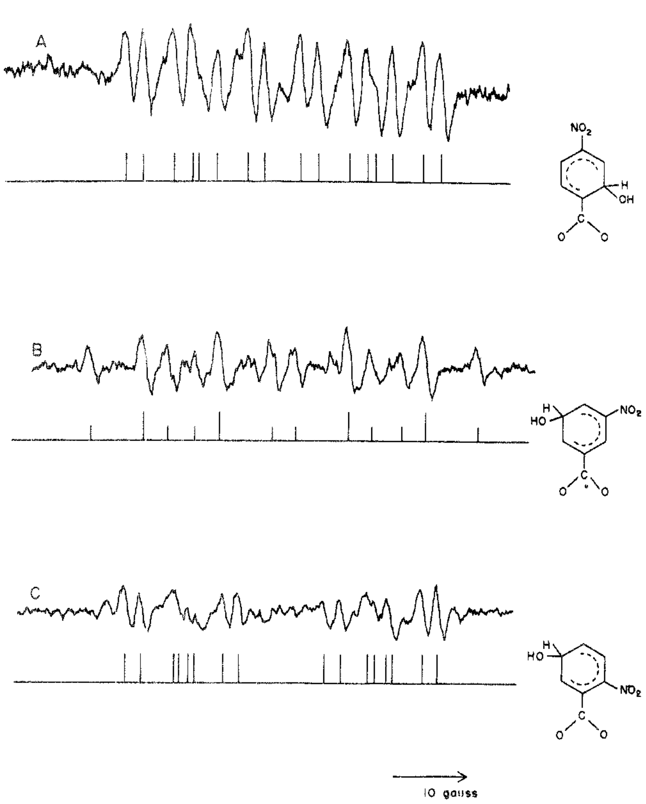


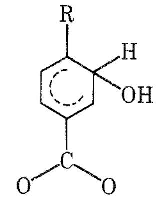
Figure 3. Epr spectra of (A) *p*-, (B) *m*-, and (C) *o*-nitrobenzoic acid radicals. Conditions: (A) and (B), modulation 100 kHz, 1.0 G, time constant 1.0 sec, scanning speed 100 G/4 min; and (C), modulation 100 kHz, 0.5 G, time constant 1.0 sec, scanning speed 100 G/4 min. The arrow at the bottom indicates the direction of the magnetic field strength, and its length corresponds to 10 G.

zoic acid free radicals consist of 16 lines, and the spectrum of *m*-nitro derivative of 12 lines which arise from 1H-1H-2H couplings.

The epr spectra of three kinds of pyridinecarboxylic acid are shown in Figure 4. The spectra of 4- and 2-substituted free radicals can easily be analyzed; the former, of isonicotinic acid free radical, consists of 26 lines originating from either 1H-1H-1N-2H or 1H-1H-1H-1H-1N couplings, and the latter, of picolic acid free radical, probably consists of 18 lines due to 1H-2H-1N couplings and other small lines. The spectrum of nicotinic acid free radical is too complicated, but may be, at best, analyzed to 48 lines as shown in the figure.

The spectrum of benzoic acid free radical is also complicated, and cannot be analyzed except for a signal of *p*-hydroxycyclohexadienyl radical, which consists of 18 lines due to 1H-2H-2H couplings. The other signals probably of meta and ortho derivatives as reported by Eiben and Fessenden,[22] cannot be separated. In addition, the shape of the spectrum did not alter with change in flow rate, *i.e.*, the ratios of the radical concentrations were the same during the 7-30 msec after mixing the solution.

In general, the signals of 16 lines can be assigned to one of the hydroxycyclohexadienyl radicals, either I or II. The large splitting of some 30 G arises from a proton attached to the sp^3 carbon of the hydroxylated position, as previously found with similar free radicals from benzene,[22,25] phenols,[27,28] benzoic acid,[22] and furans.[21] Such a large coupling constant originates from hyperconjugation with the neighboring p orbitals, but the coupling constant values of these radicals are smaller than that of the cyclohexadienyl free radical reported by Fischer[29] and others.[22,30]



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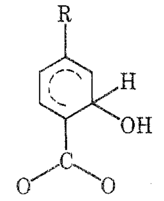

II

Comparing the hyperfine coupling constants of the benzoic acid free radicals with those of reported hydroxycyclohexadienyl radicals from benzene,[25,22] the following assignments are possible: an approximately 13-G splitting from the para proton, a *ca.* 9-G splitting from the ortho proton, and the small splitting, less than 3 G, from the meta proton (para, meta, and ortho positions with respect to the hydroxylated sp^3 carbon).

Since the fluoride hyperfine coupling is about twice as large as that of a proton, the free radical from *p*-fluorobenzoic acid (Figure 2A) is assigned structure I. The free radical from *m*-nitrobenzoic acid (Figure 4B) is a hydroxylated adduct to the meta position (with respect to the carboxylic group). Only these two radicals can be assigned structures, and the other radicals cannot be identified from the spectra without theoretical calculations.

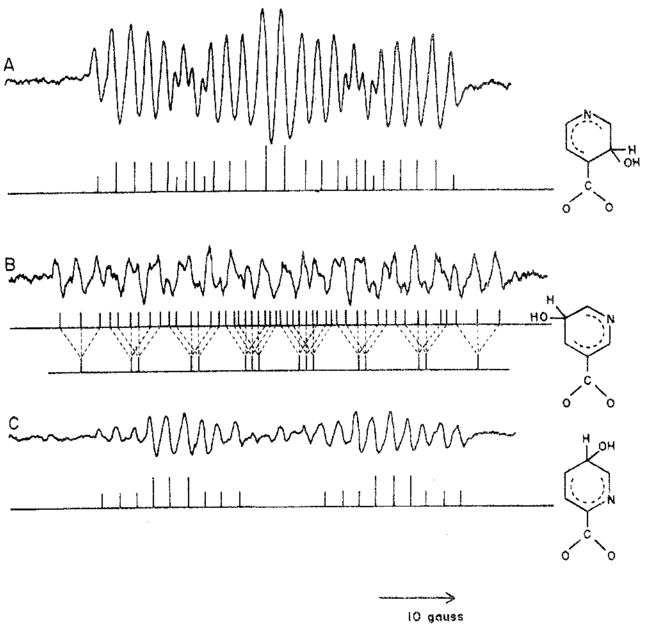

Figure 4. Epr spectra of pyridine- (A) 4-, (B) 5-, and (C) 6-carboxylic acid radicals. Conditions: (A) and (B), modulation 100 kHz, 0.5 G, time constant 1.0 sec, scanning speed 100 g/4 min; and (C), modulation 100 kHz, 0.5 G, time constant 1.0 sec, scanning speed 100 G/4 min. The arrow at the bottom indicates the direction of the magnetic field strength, and its length corresponds to 10 G.

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(28) A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc. B*, 403 (1969).

(29) H. Fischer, *J. Chem. Phys.*, **37**, 1094 (1962).

(30) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

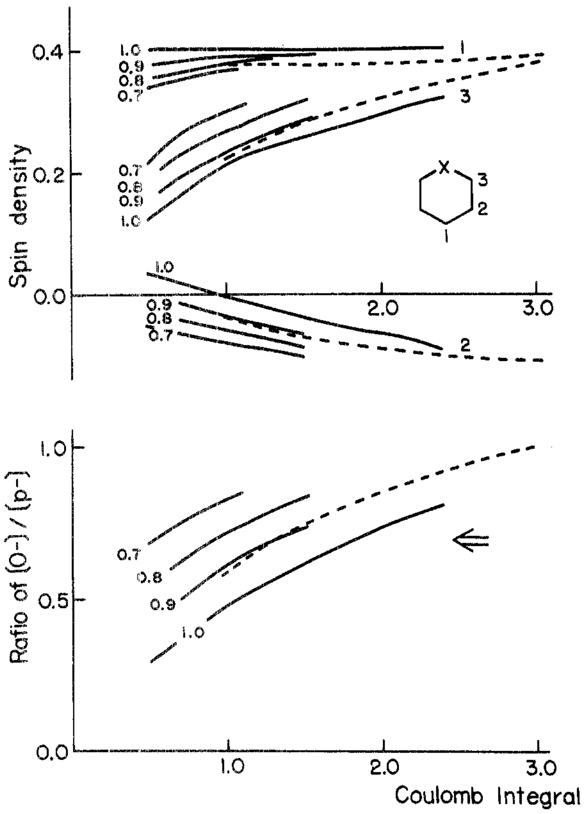


Figure 5. Plot of the Coulomb integral (δ(-CH(OH)-)) *vs.* the spin densities of the hydroxycyclohexadienyl radical: solid lines, $\delta(C') = -0.2$ and $\gamma(C-C')$ is shown in the figure; broken lines, $\delta(C') = 0.0$ and $\gamma(C-C') = 1.0$.

Calculations

In order to assign the above hyperfine couplings to molecular structures, Hückel calculations for the molecular fragments, in which the sp^3 carbon is ignored, were carried out, since this approximation has been successfully applied to the free radicals from furan derivatives.[21] However, such a simple approximation failed to support the assignment of the above structures of the identified radicals (*p*-fluoro- and *m*-nitrobenzoic acid radicals), and also failed to predict the spin densities of hydroxycyclohexadienyl radical(s), *i.e.*, the calculated spin density on the p carbon becomes smaller than that on the ortho carbon (contradiction!). Therefore, it is necessary to introduce a new set of parameters for the sp^3 carbon; assuming a planar six-membered ring with a heteroatom, the McLachlan method[31] can then be applied in order to take into account the negative spin densities.

In order to find a suitable set of Hückel parameters, the hydroxycyclohexadienyl radical[22,25,30] is taken as an example. Three parameters are varied as follows: the Coulomb integral of the sp^3 carbon (heteroatom) was taken as $1.0 \leq \delta(\text{-CH(OH)-}) \leq 3.0$; that of the neighboring carbon, $0.0 \quad \delta(\text{-C}'\text{-}) \leq -0.3$; and the bond integral between them, $0.5 \leq \gamma(\text{C-C}') \leq 1.0$. These parameters are essentially analogous to those of a methyl group treated as a heteroatom. A part of the McLachlan calculations is shown in Figure 5, where the solid lines are the spin densities of three positions, varying $\delta(\text{-CH(OH)-})$ and $\gamma(\text{C-C}')$ with fixed $\delta(\text{-C}'\text{-})$. As the best-fit parameters, $\delta(\text{-CH(OH)-}) = 2.5$, $\delta(C') = -0.2$, and $\gamma(\text{C-C}') = 1.0$ are obtained.

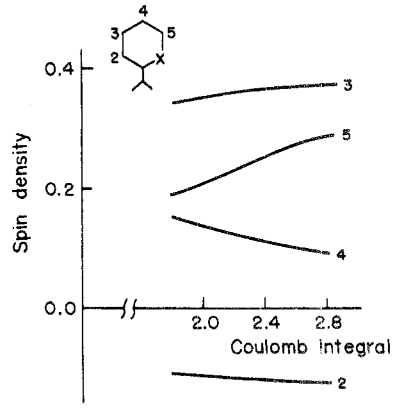


Figure 6. Plot of the Coulomb integral (δ(-CH(OH)-)) *vs.* the spin densities of the hydroxycyclohexadienyl radical from benzoic acid (ortho isomer): $\delta(C') = -0.2$ and $\gamma(C-C') = 1.0$.

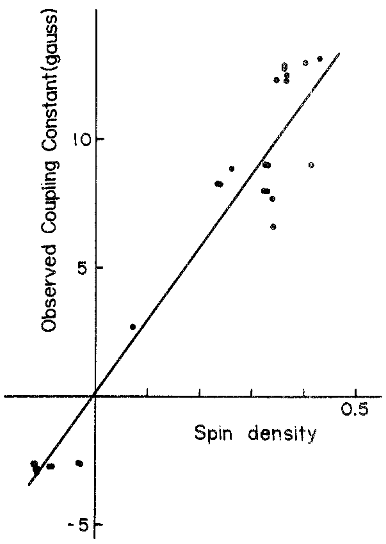
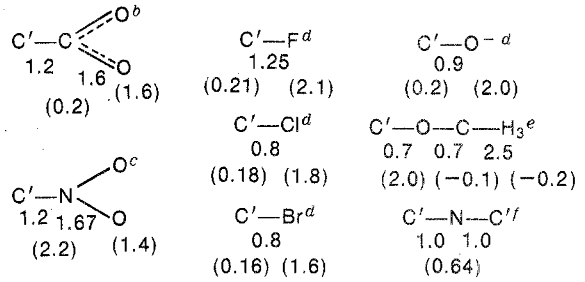


Figure 7. Plot of the calculated spin densities *vs.* observed hyperfine coupling constants.

TABLE I: Huckel Parameters[a]



C′—C(=O[b])O
1.2 1.6
(0.2) (1.6)

C′—F[d]
1.25
(0.21) (2.1)

C′—O⁻[d]
0.9
(0.2) (2.0)

C′—Cl[d]
0.8
(0.18) (1.8)

C′—O—C—H$_3$[e]
0.7 0.7 2.5
(2.0) (−0.1) (−0.2)

C′—N(O[c])O
1.2 1.67
(2.2) (1.4)

C′—Br[d]
0.8
(0.16) (1.6)

C′—N—C′[f]
1.0 1.0
(0.64)

[a] Numbers in parentheses are Coulomb Integrals, and numbers under the bond are bond integrals. [b] Slightly modified values of C. M. Moser, *J. Chem. Soc.*, 1073 (1953); and A. R. Buick, T. J. Kemp, G. T. Neal, and J. T. Stone, *J. Chem. Soc. A*, 2227 (1970). [c] Values found in ref 39. [d] Suggested values in T. Yonezawa, *et al.*, "Introduction to Quantum Chemistry," Vol. I, Kagaku-Dojin, Kyoto, 1964, p 55. [e] Values found in ref 21. [f] Values found in ref 40, which are smaller than those of C. L. Talcott and R. J. Myers, *J. Amer. Chem. Soc.*, **87**, 1651 (1965); J. C. M. Henning, *J. Chem. Phys.*, **44**, 2139 (1966); and M. D. Sevilla, *J. Phys. Chem.*, **74**, 805 (1970).

In order to obtain fine adjustment of the parameters, the calculations on hydroxycyclohexadienyl radical from benzoic acid (ortho hydroxylated)[22] were carried out. As shown in Figure 6, the spin densities are sensitive to the

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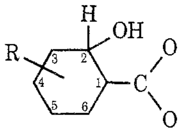
(31) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

TABLE II: Hyperfine Coupling Constants and Calculated Spin Densities[a]



R	Position attacked	CH(OH)	Para	Ortho	Meta
4-F	(3)	30.0(3)	13.1(6)	9.0(2), 19.9(4-F)	2.7(5)
		0.084	*0.431*	*0.413, 0.110*	*0.072*
4-Cl	(2)	32.8(2)	12.9(5)	8.0(3)	2.6(6)
		0.112	*0.357*	*0.330*	*−0.115*
4-Br	(2)	29.9(2)	12.8(5)	8.0(3)	2.8(6)
		0.112	*0.357*	*0.325*	*−0.114*
4-OH	(2)	29.0(2)	12.3(5)	7.7(3)	2.9(6)
		0.113	*0.355*	*0.309*	*−0.114*
4-OCH_3	(2)	29.5(2)	12.5(5)	6.6(3)	2.8(6)
		0.109	*0.364*	*0.342*	*−0.115*
4-NO_2[b]	(2)	29.8(2)	12.8(5)	8.0(3)	3.3(6)
5-NO_2[b]	(3)	34.7(3)	12.9(6)	9.0, 9.0(2,4)	
6-NO_2[b]	(4)	34.2(4)		8.5, 7.5(3,5)	2.7(2)
4-(N)[b,c]	(2)	27.6(2)	13.0(5)	8.8(3)	3.2(6),3.2(4-N)
5-(N)[b,c]	(3)	28.0(3)	20.1(6)	10.0, 8.8(2,4)	3.4(5-N)
6-(N)[b,c]	(4)	36.2(4)		8.4, 8.4(3,5)	2.8(6-N)
Benzene[d]	(4)	34.34(4)	13.1(1)	9.0(3,5)	2.7(2,6)
		0.109	*0.402*	*0.329*	*−0.084*
Benzoate[a]	(4)	34.0(4)		8.25(3,5)	2.6(2,6)
		0.102		*0.280*	*−0.030*
	(2)	34.7(2)	12.3(5)	8.9(3)	2.6(4,6)
		0.110	*0.365*	*0.263*	*−0.117*

[a] Numbers in parentheses show the positions; the coupling constants are expressed in gauss. *Italicized* numbers are the calculated densities. [b] These radicals are tentatively assigned, and in some cases, two ortho positions cannot be assigned. [c] (N) is a nitrogen substitution of the benzene ring. [d] Data from ref 22, 29, and 30. [e] Data from ref 22, which we can barely confirm and give the proton coupling constant of CH(OH) proton of ortho isomer as 34.7 G.

value of δ(-CH(OH)-). Using the above parameters, the ratios between the spin densities fit well with those of the coupling constants. However, the Q value becomes slightly larger than usual.

All possible structures of the substituted benzoic acid free radicals are calculated, using the parameters shown in Table I. The assignments of the structures can easily be made, comparing the observed coupling constants and the calculated spin densities. The results are summarized in Table II. A few radicals containing nitrogen show a systematic discrepancy between the experimental and theoretical values (see Discussion). However, the assignment of the structures can still be made; the estimated structures are shown in Table II.

Among the halogen-substituted compounds, it is seen that the hydroxylated positions are not the same for *p*-F and *p*-Cl(Br) derivatives.

The relation between the observed hyperfine coupling constants and the calculated spin densities is shown in Figure 6, in which the radicals containing nitrogen are omitted but hydroxycyclohexadienyl radicals from benzene[22] and benzoic acid (para and ortho isomers, for which we can barely confirm the analysis of Eiben and Fessenden[22]) are added. The constants of the following equations[32] are determined by a least-squares fitting.

$$A = Q\rho \qquad (1)$$

$$A = Q\rho + C \qquad (2)$$

The constants obtained were $Q = -32.3$ ($\sigma = 2.4$) G for eq 1, and $Q = -28.5$, $C = 0.1$ ($\sigma = 2.2$) G for eq 2. The Q values of various organic compounds are $-22.5 \sim -30$ G,[33] therefore the present value is within the reasonable range.

Discussion

Configuration of Intermediate Free Radicals. Generally the oxidation of benzoic acids by Fenton's reagent yields hydroxycyclohexadienyl radicals, which are the precursors of the reaction products: phenols, etc.[27,34-36] The difficulty in the structure determination from epr spectra arises from the fact that every possible structure possesses the same number of nuclei giving the hyperfine splittings. Therefore, the assignments of the structures may be ambiguous without theoretical calculations. As described in the preceding section, the assignments of the structures can be successfully made by introducing a set of new parameters for the sp^3 carbon (treated as a heteroatom).

The steric configurations of these radicals are not known. For similar molecules, the Meisenheimer salt is shown to be a planar ring; the carbon atom attached to two methoxy groups is in the usual sp^3 configuration and the distance between the sp^2 carbon and the sp^3 carbon is

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(32) H. M. McConnell, *J. Chem. Phys.*, **24**, 633, 764 (1956).
(33) A. Carrington, *Quart. Rev., Chem Soc.*, **17**, 67 (1963).
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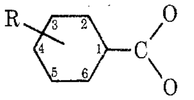
(36) C. R. E. Jefcoate, J. R. Lindsay Smith, and R. O. C. Norman, *J. Chem. Soc. B*, 1013 (1969).
(37) R. Destro, C. M. Gramaccioli, and M. Simonetta, *Nature (London)*, **215**, 289 (1967).

TABLE III: Reactive Indices



R	Position	*q*[a]	FV[b]	*L*(E)[c]	*L*(R)[c]	*L*(N)[c]	Position attacked
4-F	(2)	1.0152	0.3934	1.8211	1.8211	1.8210	
	(3)	1.0340	*0.4419*	1.5912	*1.6603*	1.7295	×
4-Cl	(2)	0.9540	*0.4187*	1.7111	*1.6295*	1.5479	×
	(3)	1.0255	0.4137	1.5899	1.6444	1.6989	
4-Br	(2)	0.9696	*0.4160*	1.7384	*1.6568*	1.5753	×
	(3)	1.0360	0.4158	1.6025	1.6665	1.7306	
4-OH	(2)	0.9714	*0.4178*	1.6894	*1.6078*	1.5262	×
	(3)	1.0267	0.4171	1.5548	1.6181	1.6815	
4-OCH_3	(2)	0.9542	*0.4155*	1.6232	*1.5413*	1.4593	×
	(3)	1.0267	0.4106	1.5577	1.5727	1.5877	
4-NO_2	(2)	0.9590	0.4272	1.5870	1.5015	1.4161	×
	(3)	0.9555	*0.4481*	1.5343	*1.3556*	1.1769	
5-NO_2	(2)	0.9320	0.4436	1.6101	1.3759	1.1412	
	(3)	0.9987	0.4011	1.5314	1.5314	1.5315	×
	(4)	0.9298	0.4453	1.5910	1.3636	1.1361	
	(6)	0.9982	*0.4667*	1.5593	*1.3232*	1.0871	
6-NO_2	(2)	0.9537	0.4304	1.5704	1.4811	1.3919	
	(3)	0.9459	0.4218	1.5806	*1.3964*	1.2122	
	(4)	1.0160	0.3843	1.5854	1.5119	1.4384	×
	(5)	0.9341	*0.4606*	1.5775	1.4153	1.2530	
4-(N)	(2)	0.9779	*0.4203*	1.5526	*1.4690*	1.3854	×
	(3)	0.9041	0.4146	1.6999	1.4982	1.2965	
5-(N)	(2)	0.8635	0.4273	1.7455	1.4711	1.1967	
	(3)	1.0077	0.3926	1.4989	1.4988	1.4987	×
	(4)	0.8352	*0.4453*	1.8092	*1.4064*	1.0037	
	(6)	0.8126	0.4362	1.7490	1.5278	1.3066	
6-(N)	(2)	0.9099	*0.4599*	1.5704	*1.2419*	0.9134	
	(3)	0.9402	0.4023	1.6716	1.4497	1.2278	
	(4)	0.9331	0.4302	1.6491	1.3473	1.0476	×
	(5)	0.8878	0.4136	2.5520	2.5173	2.4826	

[a] *q* represent electron density. [b] F$\dot{V}$ = free valence. [c] *L*(E), *L*(R), and *L*(N) are the localization energies with respect to electrophilic, radical, and nucleophilic reagents.

about 1.5 Å.[37,38] Similarly, the cyclohexadienyl radical is considered to be planar, since two proton hyperfine coupling constants of the sp^3 carbon are the same (48.08 G).[22,25] Compared with the latter radical, the introduction of a hydroxy group to the sp^3 carbon, *i.e.*, in the case of the hydroxycyclohexadienyl radical from benzene,[22,25] decreases the proton coupling constant (34.34 G).

As shown in Table II, the radicals from benzoic acids have various coupling constants (29–34 G). Such variations are also observed with radicals from phenols (24–28 G),[27] and with radicals possessing aryl groups instead of the hydroxy group (28–35 G).[28] Introducing a hydroxy group to the sp^3 carbon, the proton coupling constant due to hyperconjugation tends to decrease.

Concerning the sp^3 carbon, the relation between the proton coupling constants and the spin densities are tested by a least-squares fitting to the following equations[21,39-44]

$$A = Q(\rho(C_1') + \rho(C_2'))$$

$$A = Q_1\rho(\text{-CH(OH)-}) + Q_2(\rho(C_1') + \rho(C_2'))$$

where $\rho(C_1')$ and $\rho(C_2')$ are the spin densities on the neighboring carbons to the sp^3 carbon. However, none of these equations gives acceptable results, mainly because the deviations are too large. The following factors may be considered in explaining the variation of the coupling constants: (i) the abnormal sp^3 configuration, (ii) the nonplanality of the ring, and (iii) the electron-withdrawing effect of the hydroxy group attached to an sp^3 carbon. At the present stage, the configuration around the sp^3 carbon of the hydroxycyclohexadienyl radical cannot be estimated.

Failure of the theoretical prediction of the spin densities occurs for the nitrobenzoic acids and the pyridinecarboxylic acids. However, the four coupling constants of these radicals (*i.e.*, *ca.* 30, 13, 9, and 3 G) coincided with those of the other radicals, so that a considerable modification of the entire configuration, such as a formation of intramolecular bonding, cannot be imagined and the assignments of the structures can be made as shown in Table II. For this reason, a complex formation between the radical and iron ion is also neglected. In order to solve the discrepancy between the observed and calculated

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values, therefore, a further adjustment of the nitrogen parameters may be needed. However, our calculations are based on rough approximations, without knowledge of the real conformation. Thus a further adjustment may have no advantage. We leave this point as a future problem.

Reactive Indices and Positions of Attack. It was previously found that Fenton's reagent attacks the positions possessing maximal free valence of furan derivatives.[21] Similar tendencies are recognized with the benzoic acid derivatives. As shown in Table III, the position possessing maximal free valence and minimal localization energy against radical attack is hydroxylated, with a few exceptions. The present calculations predict the difference in position attacked between *p*-fluoro- and *p*-chloro (also bromo) benzoic acids.

In our experimental conditions, where the observations were made 7–30 msec after mixing the reactants, no change in the spectral shape was noticed within this time range with benzoic acid, which gave at least three kinds of free radicals. The whole kinetic behavior of the benzoic acid oxidation confirmed our previous description[1] of its similarity to methanol oxidation; *i.e.*, no evidence suggesting a selective annihilation of one radical and a persistence of the other[15-20] was observed in the present study. The results strongly suggest that the reactive species involved in Fenton's reagent has the character of a radical reagent.

In the cases of the nitrogen-containing compounds, in particular the pyridinecarboxylic acids, there is a possibility that the acid is complexed with the iron ion before it reacts with the reactive species. Then, the position of attack would change.

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Correlation between the n,π^* Triplet Energy of Some Ketones and Aldehydes and Their Electroreduction Potential[1]

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The n,π^* triplet energies of some aliphatic and aromatic ketones and aldehydes were found to correlate linearly with the term ($E_I - E_{1/2}^{\text{red.}} + \Delta E_{\text{soln}}$). E_I (the ionization potential) was taken to correspond approximately to the energy of the n level, and $E_{1/2}^{\text{red.}}$ (the half-wave reduction potential), to that of the π^* level. It was found that a solvation energy term, ΔE_{soln}, should be included to correct for the differences in the solvation of the compounds investigated. This linear relation can be employed to determine the triplet energy, $\Delta E_{3(\text{n},\pi^*)}$, of these carbonyl compounds whose $\Delta E_{3(\text{n},\pi^*)}$ cannot be obtained spectroscopically. The n,π^* triplet energy of acetone was calculated to be 76.6 kcal/mol, which is in good agreement with the predicted value of 75–80 kcal/mol.

Introduction

The carbonyl functionality is one of the most widely studied groups in organic photochemistry because of its role in photochemical and photobiological reactions. Hence, the triplet states of carbonyl molecules are continuing to receive considerable attention from both the experimental and theoretical points of view. Phosphorescent emission and $S_0 \rightarrow T_1$ excitation spectroscopy are the most common techniques used to determine the triplet energy levels. However, the triplet energies of a large number of carbonyl compounds have not been reported. This is quite simply due to the fact that those compounds either do not emit, or that the emission is structureless, thereby rendering an estimate of the triplet energy difficult.

A linear relationship between the n,π^* triplet energies of some benzophonones, and thiobenzophenones, and the half-wave potentials ($E_{1/2}$) was found previously[2a] and an estimate made of the position of the n,π^* triplet energies of those compounds for which n,π^* triplet states could not be observed spectroscopically.

In this paper a systematic study of the effect of substituents on the relation between the energies of the n,π^* ex-

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