Fenton's Reagent. V. Hydroxylation and Side-Chain Cleavage of Aromatics

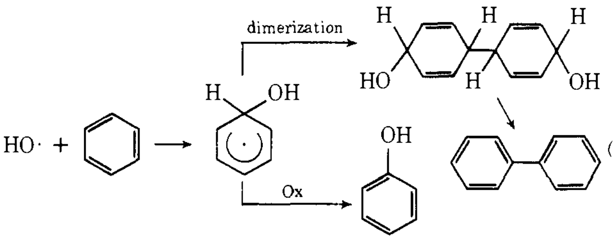
Cheves Walling* and Richard A. Johnson

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. *Received July 13, 1974*

Abstract: The reaction products of benzene, toluene, phenylacetic acid, and phenyl substituted alcohols with Fenton's reagent have been examined. Results vary widely with concentrations of H^+, Fe^{2+}, Fe^{3+}, Cu^{2+}, and O_2 and are consistent with a scheme in which hydroxyl radicals add to the aromatic system, and the resulting hydroxycyclohexadienyl radicals may dimerize, be oxidized to phenols, or undergo a reversible acid-catalyzed collapse to radical cations. These, in turn may be reduced to starting material by Fe^{2+} or, when possible, may undergo side-chain cleavage (with toluene and phenylacetic acid to benzyl radicals) followed by dimerization or further oxidation. Isomer distributions of phenolic products depend upon the oxidizing agents present, and the low yield of meta isomers obtained with Fe^{3+} is ascribed to rearrangement of intermediate hydroxycyclohexadienyl cations formed by electron transfer. Oxidation of phenylacetic acid may be directed to give phenols, bibenzyl, or benzyl alcohol with 81-94% selectivity by suitable choice of reaction conditions, and all systems gave phenols as major products in the presence of high concentrations of Cu^{2+}.

The oxidation of benzene and benzene derivatives by Fenton's reagent (Fe^{2+}-H_2O_2) has been known for over 70 years[1] and, since the pioneering mechanistic work of Merz and Waters,[2] has generated a voluminous literature. With benzene itself, data are consistent with the formation of hydroxyl radicals and their rapid addition to the aromatic ring followed by dimerization of the resulting hydroxycyclohexadienyl radicals and loss of water to yield biphenyl or by their oxidation to phenol.

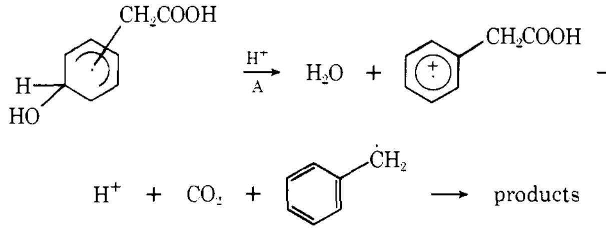
$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO^- + HO\cdot \qquad (1)$$



(2)

Radiation chemistry results have shown that the addition is very rapid (k = 3-8 × 10^9 l./mol sec),[3] and the intermediate cyclohexadienyl radical has been detected under a variety of conditions both by uv[3] and esr[4] spectroscopy. Finally, relative yields of phenol-biphenyl are increased by oxidizing agents, Fe^{3+}, Cu^{2+}, or O_2.[5,6]

Subsequent work with substituted benzene derivatives, chiefly by Norman and by Hamilton, indicates that the chemistry of hydroxyl radical adducts to aromatic systems may be considerably more complicated than indicated by (2). With Fenton's reagent and other hydroxyl radical sources, a variety of side-chain cleavage reactions have been detected, *e.g.*, phenylacetic acid yields bibenzyl, benzyl alcohol, and benzaldehyde,[7] and esr spectra of intermediates (usually obtained in flow systems in which hydroxyl radicals are generated by the Ti^{3+}-H_2O_2 reaction) indicate that both the concentration and nature of the intermediate radicals may be strongly pH dependent.[8,9] Details of these phenomena are discussed further below, but they are, in general, consistent with a scheme which can be written stepwise for the phenylacetic acid case (eq 3). However, the exact sequence is far from clear, Norman formulating steps A and B as concerted,[8] while Hamilton suggests that the intermediate radical cation is formed directly *via* hydroxyl radical attack through electron transfer.[10] This paper describes a study of the reaction of Fenton's reagent with several aromatics, chiefly benzene, toluene, and phenylacetic acid, aimed at establishing the nature of the reaction sequence in more detail.



(3)

Benzene. Our initial experiments with benzene involved the stoichiometric approach employed previously with aliphatic systems.[11,12] Here a small quantity of H_2O_2 is added to a system containing excess Fe^{2+} and substrate, and we assume that the system is described by the reactions shown in (4), *i.e.*, that radical attack on substrate yields radicals

$$
\begin{aligned}
&H_2O_2 + Fe^{2+} \xrightarrow{k_1} HO\cdot + HO^- + Fe^{3+}\\
&HO\cdot + Fe^{2+} \xrightarrow{k_2} HO^- + Fe^{3+}\\
&HO\cdot + \text{substrate}
\begin{cases}
\xrightarrow{k_{3i}} R_i\cdot \xrightarrow{Fe^{3+}} \text{product} + Fe^{2+}\\
\xrightarrow{k_{3j}} R_j \longrightarrow \text{dimerization}\\
\xrightarrow{k_{3k}} R_k\cdot \xrightarrow{Fe^{2+}} \text{product} + Fe^{3+}
\end{cases}
\end{aligned}
\qquad (4)
$$

$R_i\cdot$, $R_j\cdot$, and $R_k\cdot$ which are respectively oxidized by Fe^{3+} to regenerate Fe^{2+}, inert, and reduced by Fe^{2+} (often to regenerate starting material).

This system of equations yields the stoichiometric relation

$$R = 2ar(1 - R) + b \qquad (5)$$

where $R = \Delta[Fe^{2+}]/2\Delta[H_2O_2]$, the ratio of equivalents of Fe^{2+} oxidized to those of H_2O_2 added, or the reciprocal of the kinetic chain length, $r = [Fe^{2+}]/2[RH]$, $a = k_2/k_3$ ($k_3 = k_{3i} + k_{3j} + k_{3k}$); $b = (k_{3j} + 2k_{3k})/2k_3$.[13] For a set of experiments in which r is varied and R measured, a plot of R *vs.* $r(1 - R)$ should be linear with slope and intercept yielding a and b, respectively.

Typical data for benzene under three conditions are shown in Figure 1. With Fe^{2+} alone (*i.e.*, with only Fe^{3+} produced in the reaction present), a = 0.10, which, assuming $k_2 = 3 \times 10^8$,[3] gives $k_3 = 3 \times 10^9$ in agreement with radiation results, while b = 0.73. Experiments in the presence of 0.04 M Fe^{3+} give another line of slightly larger

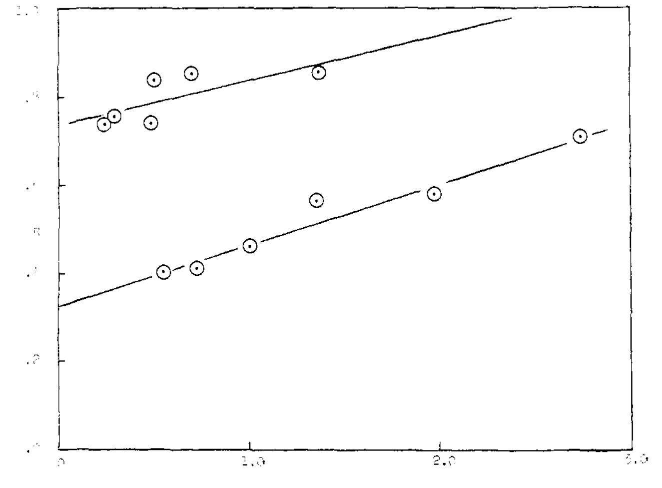


Figure 1. Plot of eq 5 for benzene. Upper curve: 0.019 M Fe^{2+}; 0.1 M H^+. Lower curves: 0.04 M Fe^{3+} added.

slope (a = 0.14) and a smaller intercept (b = 0.33) indicating that now significant radical oxidation is taking place. Experiments with 0.04 M Cu^{2+}, a better radical oxidant,[11] gave somewhat scattered results (not shown) but a value of b within experimental error of zero, indicating extensive radical oxidation and long kinetic chains.[14]

Although the stoichiometric approach yields reasonable values of k_3 and indicates a variation in b consistent with Norman's results on product distribution,[5] we find that detailed product studies yield more information in aromatic systems. Our product studies were carried out on benzene-saturated solutions (approximately 0.02 M) with excess benzene present. Phenol and biphenyl were determined by glc, and only traces of higher oxidation products could be detected, although reaction mixtures containing added Fe^{3+} or Cu^{2+} were often appreciably colored.

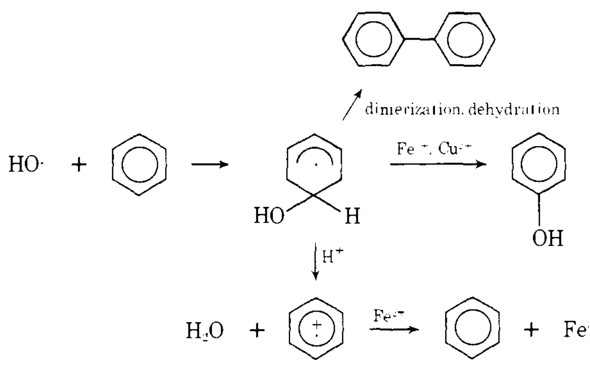
Table I shows results. In addition to yields of biphenyl and phenol, R's were also determined and compared with values calculated on the basis that phenol, biphenyl, and "unaccounted for" (see below) consume 0, 1, and 2 mol of Fe^{2+} per one mol of H_2O_2 reacted. Agreement indicated that our material balances are good.

Table I. Reaction of Benzene with Fenton's Reagent[a]

Run no.	Fe^{3+}	Cu^{2+}	H^+	% yield Phenol	Biphenyl	Total	R Found	Calcd
1			0.1	21	24	45	0.74	0.67
2			1.0	6	1	7	0.96	0.94
3	0.04		0.1	43	6	49	0.35	0.54
4	0.08		1.0	15	0	15	0.75	0.85
5		0.04	0.1	57	0.4	57	0.2	0.43
6		0.08	1.0	49	0	49	0.34	0.51
7[b]			0.1	0.2	56	56	0.66	0.72

[a] All runs 0.018 M Fe^{2+}, benzene saturated (~0.02 M). [b] 0.1 M NaF.

Qualitatively, Table I confirms Norman's findings and the implications of Figure 1. Phenol–biphenyl ratios are increased by added Fe^{3+} or Cu^{2+} and decreased by fluoride ion which complexes Fe^{3+} and reduces its oxidation potential. More significant though, total yields are considerably below 100% and are acid dependent. This can hardly arise from direct hydroxyl radical reduction by Fe^{2+} since benzene/Fe^{2+} ratios are larger than unity, and $k_3/k_2 \sim 10$. Rather, we consider our results a confirmation of the acid-catalyzed dehydration of hydroxycyclohexadienyl radicals proposed by Norman and the first clear evidence that this process occurs in the hydroxylation of benzene itself (eq 6).



(6)

Consistent with (6), at high acidities in the absence of large amounts of oxidants, most intermediate radicals collapse to the benzene radical cation and are reduced back to benzene. As a result, both products and stoichiometry are the same as though little hydroxyl radical addition had occurred. However, with large amounts of oxidants, particularly Cu^{2+}, up to half the radicals are intercepted and converted to phenol, even in 1 M acid. Norman[6] has noted that phenol–biphenyl ratios increase with acidity and has proposed that this is the consequence of an acid-catalyzed disproportionation of hydroxycyclohexadienyl radicals which provides an alternate path for phenol formation. We observe the same phenomena (*cf.* runs 1 and 2 in Table I) but believe the hypothesis is unnecessary, since the acid-catalyzed dehydration itself should decrease the concentration of hydroxycyclohexadienyl radicals, and accordingly favor their first-order oxidation over their second-order coupling, and thus account for the change.

Phenylacetic Acid. This acid was investigated in some detail as a convenient substrate with good water solubility and known to be subject to side-chain cleavage.[8] Product analyses of reactions carried out under a variety of conditions are listed in Table II. In the absence of added oxidants, extensive decarboxylation occurs, and bibenzyl is obtained in up to 54% yield in agreement with Norman's findings and (3). In the presence of oxidants, O_2, Fe^{3+}, or Cu^{2+}, the intermediate benzyl radicals are largely oxidized to benzyl alcohol as might be expected, but, more striking, high yields (up to 69%) of phenolic products are also obtained. Evidently oxidants, particularly Cu^{2+}, are able to intercept the hydroxycyclohexadienyl radicals before they collapse to radical cations, and the collapse is evidently acid dependent since yields of phenolic products are lower at higher acidities. Finally, isomer distributions among the phenolic products vary significantly with the oxidizing agent, O_2 and Cu^{2+} giving over 20% of the meta isomer, while with Fe^{3+} the fraction is 10% or less. Similar variations have been noted previously in other systems and are considered in detail below.

Toluene. Product distributions obtained with toluene shown in Table III are in qualitative agreement with those of Norman and parallel closely those obtained with phenylacetic acid. In the absence of oxidants, the major product is bibenzyl, while with Cu^{2+} it is a mixture of cresols; again cresols decrease at higher acidity, and isomer distribution varies with oxidant. Total yields, based on H_2O_2, are lower than with phenylacetic acid, perhaps because the low solubility of toluene permits significant loss of hydroxyl radicals by direct reduction by Fe^{2+}.

Table II. Reactions of Phenylacetic Acid with Fenton's Reagent[a]

Run no.	[Fe^{3+}]	[Cu^{2+}]	BzOH	$(Bz)_2$	Phenols	Total	Phenol isomer distribution Ortho	Meta	Para
1			12	54	1	67			
2	0.04		32	22	5	59			
3	0.08		42	12	6	60	(90)[h]	(5)[h]	(5)[h]
4[b]	0.08		25	19	5.3	49	(90)[h]	(5)[h]	(5)[h]
5[c]	0.08		53	6.4	8.8	68	73	10	17
6	0.16		60	6	7	73	91	6	3
7		0.04	41	0.4	33	74	66	27	7
8		0.04	49	0.2	32	81	69	25	5
9[b]		0.04	36	3	16	55	80	20	0
10[c]		0.04	43	0	40	83	60	26	14
11		0.08	27	0	47	74	60	29	11
12[e]		0.08	4	0	69	73	45	31	24
13		0.16	17	0	50	67	58	31	11
14[d]		0.16	58	0	15	73	77	21	2
15		0.24	23	0	55	78	55	31	14
16[f]			2	3	7	12	66	34	0
17[g]			2	13	6	21	68	32	0

[a] All 0.05 *M* $HClO_4$, 0.02 *M* Fe^{2-}, 0.06 *M* phenylacetic acid unless indicated. [b] 0.06 *M* Fe^{2+}. [c] Inverse addition ([Fe^{2+}] ~ 0). [d] 0.25 *M* $HClO_4$. [e] 0.02 *M* NaOAc added. [f] 0.036 *M* Fe^{2-}, O_2 saturated. [g] 0.03 *M* Fe^{2+}, 0.082 *M* NaF, O_2 saturated. [h] Approximate values.

Table III. Reactions of Toluene with Fenton's Reagent[a]

Run no.	Fe^{2+}	Cu^{2+}	% yield BzOH	$(Bz)_2$	Cresols	Total	Cresol isomers Ortho	Meta	Para
1			5 (3)	22	2	35	46	0	54
2[b]			2	22	3	27	60	3	37
3[c]			6 (6)	18	0.4	36			
4	0.08		5 (5)	1	7	23	53	2	45
5	0.16		11 (6)	0.1	6	29	54	3	43
6		0.24	4 (2)	0	18	26	59	12	29
7[d]			0	36	0.5	37	64	19	17
8[e]			10 (0.3)	0	11	22	46	36	18
9[e]	0.16		9 (2)	0	11	24	55	22	23
10[f]							35	57	8

[a] All runs 0.05 *M* $HClO_4$, 0.016–0.018 *M* Fe^{3+}, toluene saturated except as indicated. Yields in parentheses under BzOH are for benzaldehyde. [b] 0.02 *M* AcO^-. [c] 0.5 *M* $HClO_4$. [d] 0.1 *M* NaF. [e] 0.032 *M* Fe^{2+}, O_2 saturated. [f] 0.02 *M* Fe^{2+}, 0.1 *M* NaF, O_2 saturated, no H_2O_2.

Other Aromatics. Table IV lists results with some phenyl-substituted alcohols of the sort investigated by Snook and Hamilton.[10] In their experiments, only side-chain cleavage products were reported, but our results show that in every case significant yields of phenolic products can be obtained in the presence of Cu^{2+}.

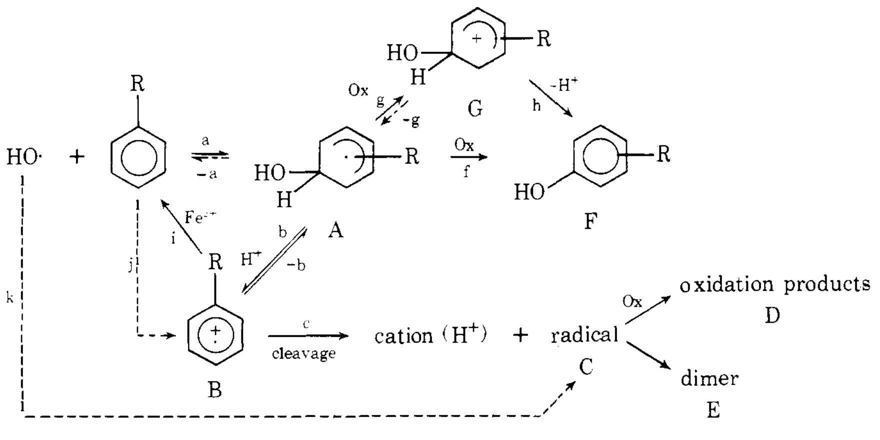
Table IV. Reactions of Phenyl Alcohols with Fenton's Reagent[a] and 0.24 *M* Cupric Ion

Substrate	% yield of phenolic products	Phenolic isomer distribution Ortho	Meta	Para
$PhCH_2OH$[b]	21	50	36	14
$PhCHOHCH_3$[c]	26	42	40	18
$PhCH_2CH_2OH$[d]	40	48	24	28

[a] 0.02 *M* Fe^{2+}, 0.24 *M* Cu^{2-}, 0.05 *M* $HClO_4$. [b] 0.15 *M* benzyl alcohol. [c] 0.06 *M* α-phenethyl alcohol, also found *ca.* 54% yield of acetophenone. [d] 0.075 *M* β-phenethyl alcohol, also found 22% yield of benzyl alcohol.

Discussion

Our previous equations for hydroxyl radical reactions with aromatics may be combined in more general form (eq 7) with steps and intermediates lettered for purposes of discussion.

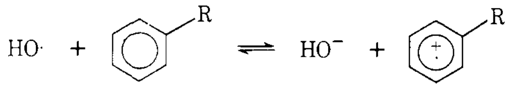


(7)

The bulk of our discussion will be based on our phenylacetic acid results, where C represents the benzyl radical and D and E benzyl alcohol and bibenzyl, respectively, with variations in other systems noted. Steps for which we believe there is substantial evidence are indicated by solid arrows, others which are also discussed by dashed arrows.

First, we conclude that most, if not all, hydroxyl radical attack on aromatics occurs *via* addition, a, to yield hydroxycyclohexadienyl radicals, A. This is in agreement with Norman's conclusions and the frequent detection of A by spectroscopic means and is strongly supported by our own finding that phenolic products can be detected in every system in the presence of adequate oxidant, particularly Cu^{2+}, and can often be made the major products. This shows that direct side-chain attack, k_l, cannot be more than a minor reaction path. A further argument, as Hamilton has pointed out for benzyl alcohol systems, is that the rates of hydroxyl radical reactions with aromatics are much faster than would be anticipated for side-chain hydrogen abstraction. Thus for benzyl alcohol,[3] the rate constant has been reported as 8.4×10^9. Toward similar electrophilic radicals, chlorine atoms and alkoxy radicals, benzylic hydrogens are less reactive than allylic, and our data on allyl alcohol[12] show that, toward hydroxyl radicals, allylic hydrogens are if anything less reactive than their saturated analogs. Accordingly we would anticipate a rate constant for side-chain attack on toluene of $<10^9$. With phenylacetic acid, the arguments against side-chain attack have already been given in detail by Norman.[7]

In order to account for an apparent high reactivity of aromatic alcohols compared with benzene, Hamilton[10] has proposed either path j (perhaps concerted with c) or initial formation of a π complex. We believe the strongest argument against direct electron transfer, j, is an energetic one. The reduction potential of HO· is approximately 1.0 V, while the oxidation potential of typical alkyl benzenes are 1.8–2.0 V. Accordingly, the equilibrium in eq 8 must lie far to the left, and its rate to the right should be slow. In the sequence a,b, this difficulty is ameliorated since water, rather than HO^-, is a product. The π-complex scheme, while compatible with our results, introduces an additional intermediate for which there is only questionable evidence,[15] and which must rapidly be converted to the species which we discuss.

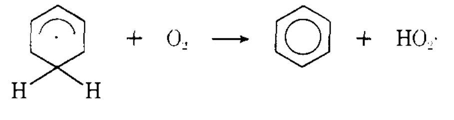


(8)

If A represents the primary product of hydroxyl radical attack, a step such as b is required to account for cleavage products, and its acid dependence seems well established. We prefer to regard B, the radical cation, as a bona fide intermediate, rather than formulating b and c as concerted, chiefly because it provides a means (*via* Fe^{2+} reduction, i) of accounting for the "missing products" (20–70% depending on the system) based on H_2O_2 and because of the decrease in total product yield with increasing Fe^{2+} concentration (see below). Further "collapse" occurs with benzene and other molecules such as anisole[8,9] in which no side-chain cleavage is possible.

If our scheme is correct, the effect of Fe^{2+} on total yield and product distribution also suggests that b, the collapse to radical cation, is also reversible so that yields of phenols decrease with increasing Fe^{2+} (compare runs 3, 4, and 5 and runs 8, 9, and 10 in Table II). Such a process, −b, would represent nucleophilic attack by water on the radical cation. Nucleophilic attack on aromatic radical cations has been noted in other systems,[16] and for benzene hydroxylation, is supported by isotope exchange experiments with ^{18}O-enriched water.[17] Incidentally, it should be noted that the interconversion of A and B as formulated is mechanistically identical with the acid-catalyzed equilibration of, *e.g.*, *tert*-butyl alcohol and the *tert*-butyl carbonium ion, the only difference being that here both species are also free radicals.

Finally we must consider the nature of the oxidation steps f and g and, in particular, account for the changes in isomer distribution observed in different systems. Reaction of the unsubstituted cyclohexadienyl radical by molecular oxygen in nonaqueous media has been shown convincingly by Ingold[18] to involve a simple homolytic displacement, and we propose that the same process occurs in our systems,

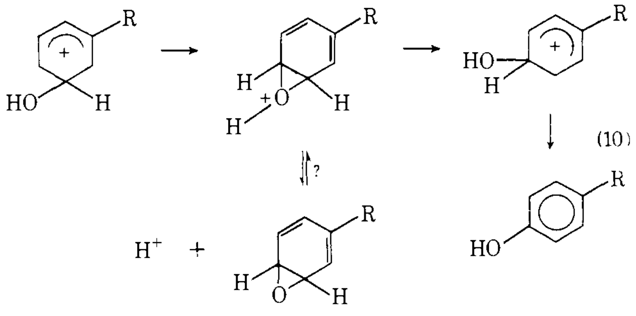


(9)

with the resulting $HO_2\cdot$ radical being either reduced to H_2O_2 or oxidized to O_2 depending upon the relative concentrations of Fe^{2+} and Fe^{3+} plus Cu^{2+} present. The relatively low yields of total products often observed in oxygen saturated systems (*cf.* runs 16 and 17 in Table II), however, represent some wastage of hydrogen peroxide which we do not understand.

From all tables, Cu^{2+} is clearly the most effective oxidant for hydroxycyclohexadienyl radicals, and we assume that reaction proceeds *via* an organocopper intermediate as proposed by Kochi for simple alkyl radicals.[19] Isomer distributions of phenolic products are very similar to those observed with O_2 and we believe reflect essentially the relative concentrations of cyclohexadienyl radicals A; in short, with both O_2 and Cu^{2+}, path 8 is followed. However, it should be noted that, to the extent that path −b occurs, this is an *equilibrium* distribution rather than that determined *kinetically* by hydroxyl radical addition.

We have previously presented arguments that radical oxidations by Fe^{3+} are outer-sphere electron-transfer processes, giving rise to carbonium ion type products.[11,12] We propose that the same is the case here so that Fe^{3+} oxidations follow path g, and that this accounts for the change in isomer distribution (decreased amounts of meta-substituted phenols) observed. Since Fe^{3+} oxidations are highly sensitive to the stability of the resulting carbonium ion species, and overall yields in both Tables II and III are low, this could be due to selective oxidation of ortho- and para-substituted hydroxycyclohexadienyl radicals which should yield the more stable carbonium ions. However, since benzene itself, with no carbonium ion stabilizing substituents, gives almost as high phenol yields with Fe^{3+} as with Cu^{2+}, this explanation appears doubtful. We prefer to propose that, instead, we are seeing rearrangement of the intermediate carbonium ions to their most stable isomers, *e.g.*, as shown in eq 10. We have no evidence for the actual formation of



(10)

epoxide (which should immediately reopen in an acid media), but it is plain that our formulation is similar to that proposed for intermediates in reactions involving "NIH shifts."[20]

Although any reaction scheme as complex as (7) is very difficult to confirm quantitatively in complete detail, all steps are ones which have been postulated or demonstrated in other systems, and it accounts very satisfactorily for the bulk of our results. It serves to illustrate the extreme complexity of the reaction of hydroxyl radicals with aromatics and the difficulties in drawing mechanistic conclusions from (particularly partial) product analyses under a limited range of experimental conditions. As examples, it is plain that conclusions on the role of hydroxyl radicals in aromatic hydroxylations on the basis of the distribution of phenolic isomers require at least a careful definition of experimental conditions. Similarly, conclusions as to substitution patterns by hydroxyl radicals or the electrophilic properties of the hydroxyl radical based on relative reactivity data may be highly suspect since equilibration, rearrangements, and reversion to starting material may all be occurring to varying degrees. As examples of these difficulties, ortho,para-substitution and NIH shifts have been taken as evidence for two electron oxidations by "positive oxygen" or "oxene." However, our scheme implies that the same results can occur *via* two successive one-electron processes yielding a hydroxycyclohexadienyl cation and can be observed in radical additions providing a suitable one-electron transfer oxidant is present.[21]

On the other hand, it is plain that our model permits the control of the Fenton's reagent reaction to give very high selectivity to specific products. In the case of phenylacetic acid, from 81% bibenzyl or 82% benzyl alcohol to 94% phenolic derivatives.

Experimental Section

Reactions were carried out by slowly adding H_2O_2 to stirred solutions of other reactants, substrate, $HClO_4$, and perchlorate salts, (under N_2 unless indicated) essentially as in our previous papers.[11,12] In inverse additions, Fe^{2+} was added to systems containing H_2O_2. Stoichiometric studies with benzene were carried out below saturation, but in product studies with benzene and toluene solutions were kept saturated by adding excess substrate to maintain a second phase.

Analyses of products were by glc [usually after prior silylation with *N,O*-bis(trimethylsilyl)acetamide (BSA)] using 10-ft 5% SE-30 columns on Chromosorb W, a flame ionization detector, and oven temperatures programmed from 80 to 200°. Results were made quantitative by the use of added internal standards and instrument response calibration with known mixtures. Specific systems are described further below.

Benzene. Method A: Reaction mixtures were extracted with four portions of chloroform, the extracts dried, α,α-dimethylbenzyl alcohol added as internal standard, and analyzed. Method B: Reaction mixtures were extracted with four portions of ether, the extract dried, *m*-cresol added as internal standard, and excess BSA added to an aliquot. After standing for a few minutes, the aliquot was analyzed by glc.

Phenylacetic Acid. Reaction mixtures were saturated with $(NH_4)_2SO_4$, made 1 *M* in H_2SO_4, and extracted with ether as above. The extract was dried, silylated, and analyzed using *o*-terphenyl as an internal standard. The silylated hydroxyphenylacetic acids separated cleanly, appearing in the order ortho, meta, para as established using known standards.

Toluene. Because of poor separation of silylated benzyl alcohol and cresols, the latter were separated before analysis. Ether extract of reaction mixtures were extracted with 0.1 *M* NaOH (three portions), dried, treated with BSA, and analyzed for benzyl alcohol, benzaldehyde, and bibenzyl using biphenyl as internal standard. The NaOH extract was acidified, extracted with ether, dried, and phenol added as an internal standard. The volume of extract was reduced on a rotary evaporator, and an aliquot silylated and analyzed. The silylated cresols separated cleanly, again eluting in the order ortho, meta, para.

Benzyl and phenylethyl alcohols products were analyzed in the same manner as those from phenylacetic acid. The order of elution of silylated phenolic products was assumed the same as with products from phenylacetic acid and toluene, so identifications are somewhat tentative.

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(13) Equation 5 was originally derived for the case of aliphatic molecules where different points of hydroxyl radical attack yielded radicals with different properties. However, it can also be applicable to situations where a single radical undergoes competing reactions. If the competition is not affected by *r*, *b* is then determined by the fractions of radicals which are oxidized, inert, or reduced.
(14) The slope *a* is also larger, a phenomenon also noted in some alcohol oxidations[12] and there attributed to some trapping of hydroxyl radicals by Cu^{2+} which can make determinations of k_3 unreliable under these conditions.
(15) The evidence is a reported[10] relative reactivity (based on product yields) of 2 for benzene:isopropyl alcohol compared with 3.7:11 (chiefly 4-5) for aromatic alcohols:isopropyl alcohol. However, compared with radiation results,[3] the aromatic alcohol results are typical for aromatic molecules, and the benzene result is low. Part of the difficulty may be that benzene yields are not quantitative; *cf.* Table I.
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(20) For a recent review of such reactions, *cf.* D. M. Jerina, *Chem. Technol.*, 120 (1973).
(21) This same argument has been made by Norman,[6] although the small amount of NIH shift which he reports with *p*-deuterioanisole does not correlate in any expected manner with the oxidants present.