400.18860; found, m/e 400.18855.

9-*O*-Methylkalafungin. Trifluoroacetic acid (two drops) was added to a solution of **14** (120 mg, 0.30 mmol) in dichloromethane (1.0 mL) cooled to 0 °C under nitrogen. The cooling bath was removed and the red solution stirred 1 h at ambient temperature. Toluene (10 mL) was added and the solvents were removed at reduced pressure (repeated 3 times). The residue was dissolved in benzene (3 mL) and then cooled to 5 °C. Diazabicyclononane (2 drops) was added and stirring continued for 10 min. Ether (10 mL) was added and the solution transferred to a separatory funnel, where it was washed with ice-cold 0.25 N HCl (2 × 5 mL) and brine (10 mL). The dried (Na_2SO_4) solution was filtered and concentrated to afford a yellow oil. The oil (95 mg) was dissolved in THF (3 mL), and argentic oxide (150 mg, 1.15 mmol) was added followed by 0.3 mL of 6 N HNO_3. Stirring was continued for 10 min. Then 4:1 $CHCl_3/H_2O$ (10 mL) was added. After transfer to a separatory funnel, the whole was extracted with $CHCl_3$ (2 × 50 mL), and the organic layer was then washed with water (2 × 5 mL) and brine (5 mL). The dried solution was filtered and concentrated. The residue was chromatographed (silica gel, 1:1 hexane/ethyl acetate) to afford 42 mg of an orange solid: mp 203–210 °C dec (from acetone); R_f (1:1 hexane/ethyl acetate) 0.15; IR (Nujol) 1780, 1665 cm^{-1}; 90-MHz NMR ($CDCl_3$) δ 1.55 (d, 3 H, J = 7 Hz), 2.63 (d, 1 H, J = 18 Hz), 2.98 (dd, 1 H, J = 18 and 5 Hz), 4.02 (s, 3 H), 4.68 (dt, 1 H, J = 5 and 3 Hz), 5.05 (q, 1 H, J = 7 Hz), 5.27 (d, 1 H, J = 3Hz), 7.2–8.0 (m 3 H); 90-MHz C 13 NMR ($CDCl_3$) δ 18.636, 36.947, 56.504, 66.417, 66.905, 68.909, 118.208, 119.563, 132.510, 133.865, 135.598, 151.038, 160.139, 174.062, 182.513, 203.371; UV (CH_3OH) 211, 253 nm. High-resolution mass spectrum for $C_{17}H_{14}O_6$ required m/e 314.07904; found, m/e 314.07856.

Kalafungin (3). Excess boron trichloride was added to 9-*O*-methylkalafungin in 1 mL of anhydrous dichloromethane cooled to −78 °C under nitrogen. When addition was complete, the cooling bath (dry ice–acetone) was removed and the bright purple solution was allowed to warm to ambient temperature. Ten minutes after removing the cooling bath, water was added with vigorous stirring. The yellow-orange solution was diluted with dichloromethane (50 mL) and washed with water (2 × 10 mL) and brine (10 mL). The dried solution was filtered and concentrated to provide **3** as light orange crystals.

Pachybasin (15). To a solution of 0.97 g (4.0 mmol) of the hydroquinone **16** in 20 mL of CCl_4 was added 0.71 g (4.0 mmol) of NBS and a catalytic amount of benzoyl peroxide. The mixture was refluxed for 10 $^1/_2$ h. On cooling to room temperature, a solid precipitated out of solution. The reaction mixture was diluted with ethyl acetate, washed with water and then brine, and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was chromatographed on silica gel using 2:1 hexane/CH_2Cl_2 as solvent to give 0.46 g (1.92 mmol), 48%) of pachybasin (**15**): NMR ($CDCl_3$) δ 2.40 (s, 3 H), 7.00–8.40 (m, 6 H); IR (Nujol) 1670, 1640, 1590 cm^{-1}; mp 178–180 °C (lit.[25] 176–177 °C).

General Procedure for Annulations with *t*-BuOK. To a solution of 1.0 equiv of the requisite phthalide and 1.0 equiv of the α,β-unsaturated ketone in dry Me_2SO (0.25 M) was added 3.0 equiv of potassium *tert*-butoxide/*tert*-butyl alcohol complex in three equal portions over 4 h from 0 °C to 25 °C. The reaction mixture was then acidified with aqueous HCl and extracted 4 times with ether. The organic layer was washed with water and brine, dried over sodium sulfate, filtered, and concentrated in vacuo. The crude product was chromatographed on silica gel.

1-Hydroxy-8-methoxy-3-methylanthraquinone: mp 186 °C; NMR ($CDCl_3$) δ 2.40 (s, 3 H), 4.02 (s, 3 H), 6.97–8.00 (m, 5 H).

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Registry No. **3**, 11048-15-0; **4a**, 51287-54-8; **4a** 2-cyclohexenone adduct, 80301-48-0; **4a** 5-(trimethylsilyl)-2-cyclohexenone adduct, 86823-73-6; **4a** 5-methyl-2-cyclohexenone adduct, 80301-50-4; **4a** 3-penten-2-one adduct, 40420-49-3; **4b**, 27613-27-0; **4c**, 73318-26-0; **4d**, 81060-27-7; **5a**, 6520-83-8; **5b**, 86823-74-7; **5b** 5-methyl-2-cyclohexenone adduct, 86823-75-8; **5c**, 86823-76-9; **5c** 5-methyl-2-cyclohexenone adduct, 86823-77-0; **5d**, 81625-31-2; **6**, 6555-40-4; **7**, 83662-31-1; **9**, 86823-78-1; **13**, 86823-79-2; **14**, 86823-80-5; **15**, 2549-78-2; **16**, 80301-50-4; PhCH=CHCOPh, 94-41-7; ethyl 6-methyl-2-oxocyclohex-3-encarboxylate, 78073-67-3; ethyl 2-(bromomethyl)-6-methoxybenzoate, 86823-81-6; ethyl 2-(bromocyanomethyl)-6-methoxybenzoate, 86823-82-7; 7-methoxyphthalide, 28281-58-5; 5-methyl-2-cyclohexenone, 7214-50-8; 5-(trimethylsilyl)-2-cyclohexenone, 56917-71-6; 2-cyclohexenone, 930-68-7; 3-penten-2-one, 625-33-2; ethyl acrylate, 140-88-5; methyl vinyl ketone, 78-94-4; 2-acetyl-8-methoxy-1,4-naphthoquinone, 81418-42-0; furan, 110-00-9; 2-*tert*-butoxyfuran, 32460-41-6; 9-*O*-methylkalafungin, 23125-83-9; 1-hydroxy-8-methoxy-3-methylanthraquinone, 3300-25-2; 2(5*H*)-furanone, 497-23-4; ethyl 1,4-dihydroxynaphthalene-2-carboxylate, 66928-23-2; 4,9-dihydroxynaphtho[2,3-*c*]furan-1(3*H*)-one, 68726-79-4; 2-benzoyl-3-phenyl-1,4-naphthalenediol, 1169-61-5; 3,4-dihydro-2*H*-anthracene-1,9,10-trione, 52422-35-2; chrysophanol, 481-74-3.

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Formation of OH Radicals from Radical Cations of Some Substituted Benzenes in Aqueous Solutions at 80 °C and at Room Temperature. Effect of Oxygen[1]

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The reactions of a number of simple substituted-benzene radical cations with water at 80 °C and at room temperature have been investigated. The radical cations were produced by thermal decomposition of $Na_2S_2O_8$. We searched for the formation of OH radicals, which we identified by their reaction with nitrobenzene to give nitrophenols. The thermal decomposition of peroxydisulfate in deoxygenated, nitrobenzene-saturated aqueous solutions of chlorobenzene, bromobenzene, and *tert*-butylbenzene gave *o*- and *p*-nitrophenols, whereas fluorobenzene, iodobenzene, phenol, and chlorophenols gave no nitrophenols. With nitrobenzene alone, no nitrophenols were obtained. The structural requirements for the reaction of aromatic radical cations with water to produce OH radicals are discussed. In the presence of oxygen, the yield of chlorophenols and bromophenols increased dramatically, producing mainly the para isomer, but in the bromobenzene case also significant amounts of *m*-bromophenol. The mechanism of this oxidation is discussed.

We have recently reported a reaction between benzene radical cations and water to give OH radicals.[2,3] This reaction was found to occur at temperatures as low as 25 °C[3] in the absence of oxygen or oxidizing metal ions. We

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Table I. Thermal Decomposition of $S_2O_8^{-2}$ in Aqueous Solutions of Fluorobenzene[a]

reactants, M		products, mol × 10^5			
			nitrophenols		
PhF	$PhNO_2$	phenol	ortho	meta	para
10^{-2}	0	20.8			
10^{-2}	9.4×10^{-3}	27.7	1.5	0	0.7

[a] Concentration of $S_2O_8^{2-}$ was 4.5×10^{-3} M in all experiments. [b] Both experiments were carried our for 1 h at 80 °C under an Ar atmosphere.

suggested that the benzene radical cation adds water to form a hydroxycyclohexadienyl radical, which in turn can dissociate to benzene and OH radical.

We have also shown that no OH radicals are formed from the radical cations of toluene and anisole. In order to obtain further examples of OH radical formation from aromatic radical cations, we have investigated a number of substituted-benzene radical cations in aqueous solutions.

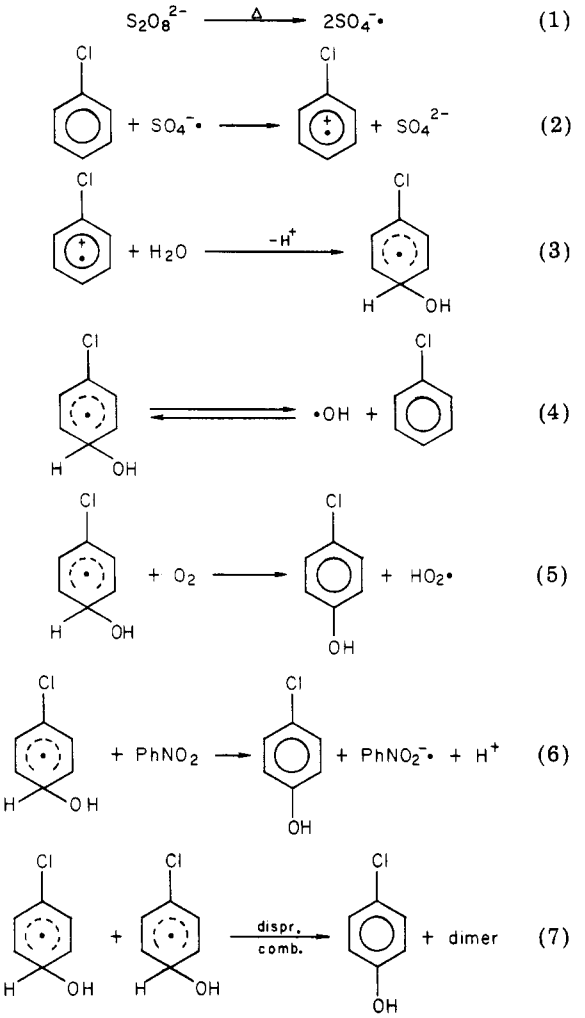
Results

We have studied the thermal decomposition of $Na_2S_2O_8$ in deoxygenated and oxygenated aqueous solutions of fluoro-, chloro-, and bromobenzene. We have used the formation of nitrophenols from nitrobenzene as an OH radical probe. The results of these experiments are summarized in Tables I–III. In the experiments with fluorobenzene (Table I) in deoxygenated solutions, only trace amounts of nitrophenols were formed, while with chloro- and bromobenzene (Tables II and III) we found considerable amounts of nitrophenols both at 80 °C and at room temperature. In these experiments, oxygen had a considerable effect on the product yields. The chloro- and bromophenols increased; whereas the nitrophenol yield decreased. A similar effect of oxygen was observed by us in our previous work on benzene radical cations,[2,3] where oxygen increased the yield of phenol and decreased the yield of nitrophenol to almost zero. In addition to the experiments listed in Tables I–III, we have studied the thermal decomposition of $Na_2S_2O_8$ in deoxygenated aqueous solutions of iodobenzene (10^{-2} M), phenol (4×10^{-3} M), and *o*-, *m*-, and *p*-chlorophenol (4×10^{-3} M) in the presence of nitrobenzene. In none of those experiments did we find any formation of nitrophenol. In another experiment analogous to experiment 2 in Table I, but with *tert*-butylbenzene (6.4×10^{-3} M), we obtained 10.0×10^{-5} mol of *o*-nitrophenol and 4.4×10^{-5} mol of *p*-nitrophenol.

Discussion

The thermal decomposition of peroxydisulfate leads to $SO_4^{-\cdot}$, which reacts with aromatic compounds to give radical cations.[4-10] It has been established that radical cations of some aromatic compounds react in aqueous solutions in the presence of oxidizing agents to give phenol and substituted phenols.[11,12] These phenols are produced via an intermediate hydroxycyclohexadienyl radical, which in absence of oxygen can dissociate to give OH radicals, analogous to our previously described reaction between benzene radical cations and water.[2,3]

Scheme I



The mechanism for these reactions with chloro- and bromobenzene is summarized in Scheme I. The addition of water to these radical cations takes place preferentially at the para position. This can be concluded from the almost total absence of phenol in our experiments and the dramatic increase in *p*-chlorophenol and *p*-bromophenol in the presence of oxygen. These results are in agreement with those obtained by Walling et al.[13] These authors have shown that in the reaction of chlorobenzene radical cation with water in the presence of Cu^{2+}, mainly *p*-chlorophenol is formed, with smaller amounts of the ortho- and maximally only 3% of the meta isomer. In absence of oxygen or oxidizing metal ions, the para OH adduct dissociates to the aromatic and OH radicals, which we have identified by its reaction with nitrobenzene to give nitrophenols. On the basis of the results of Neta et al.,[10] one can estimate that the rate constants for the reaction of $SO_4^{-\cdot}$ with the aromatics examined in the present work are

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Table II. Thermal Decomposition of $S_2O_8^{2-}$ in Aqueous Solutions of Chlorobenzene[a]

reactants, M		conditions		products, mol × 10^5					
				chlorophenols			nitrophenols		
PhCl	$PhNO_2$	temp, °C	time	ortho	meta	para	ortho	meta	para
5×10^{-3}	0	Ar 25	10 days	3.7	2.2				
5×10^{-3}	4.7×10^{-3}	Ar 25	10 days	5.5	2.3		4.5		2.0
5×10^{-3}	0	O_2 25	10 days	4.6	0.5	24.0			
5×10^{-3}	4.7×10^{-3}	O_2 25	10 days	3.4	29.5		1.0	0.3	0.6
10^{-2}	0	Ar 80	1 h	4.7	4.9				
10^{-2}	9.4×10^{-3}	Ar 80	1 h	6.2	4.9				
10^{-2}	0	O_2 80	1 h	7.0	2.0	24.5			
10^{-2}	9.4×10^{-3}	O_2 80	1 h	5.3	24.7		1.3	0.7	0.8

[a] The chlorobenzene and nitrobenzene at the higher concentrations did not dissolve completely. Concentration of $S_2O_8^{2-}$ was 4.5×10^{-3} M in all experiments. The experiments at 25 °C were carried out in 1 L and the experiments at 80 °C in 500 mL of solution. Ar: argon bubbled through the solution for 30 min (500 mL solutions) and 40 min (1 L solutions) before addition of the aromatics. O_2: oxygen bubbled through the solution for 30 min. Only traces of phenol were detected in any of the above experiments.

Table III. Thermal Decomposition of $S_2O_8^{2-}$ in Aqueous Solutions of Bromobenzene[a]

reactants, M			products, mol × 10^5					
			bromophenols			nitrophenols		
PhBr	$PhNO_2$	conditions	ortho	meta	para	ortho	meta	para
5×10^{-3}	0	Ar, 25 °C 10 days	2.3	trace				
5×10^{-3}	4.7×10^{-3}	Ar, 25 °C 10 days	4.2	1.4		3.5		1.5
5×10^{-3}	0	O_2, 25 °C 10 days	2.1	1.0	9.1			
5×10^{-3}	4.7×10^{-3}	O_2, 25 °C 10 days	2.0	11.2		2.5	1.2	1.0
10^{-2}	0	Ar, 80 °C 1 h	1.8	1.0				
10^{-2}	9.4×10^{-3}	Ar, 80 °C 1 h	3.0	2.6		14.0		7.1
10^{-2}	0	O_2, 80 °C 1 h	3.6	3.5	12.9			
10^{-2}	9.4×10^{-3}	O_2, 80 °C 1 h	2.4	13.4		3.2	1.5	1.5

[a] The bromobenzene and nitrobenzene at the higher concentrations did not dissolve completely. The concentration of $S_2O_8^{2-}$ was 4.5×10^{-3} M in all experiments. The experiments at 25 °C were carried out in 1 L and the experiments at 80 °C in 500 mL of solution. Only traces of phenol were detected in any of the above experiments.

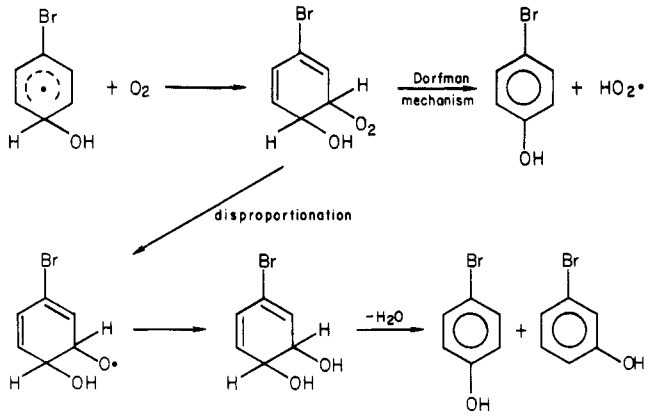
in all cases $>10^8$ M^{-1} s^{-1}, whereas the rate constant with nitrobenzene is $<10^6$ M^{-1} s^{-1}. In all our experiments, therefore, >99% of $SO_4^{-\cdot}$ reacts initially with the substituted benzene and not with nitrobenzene. As we have argued in our previous work, the formation of nitrophenols can only be due to a reaction with OH radicals. If only nitrobenzene is present, no nitrophenols are formed.

In our present experiments with chloro- and bromobenzene radicals cations, we obtain in the presence of oxygen in addition to the para-substituted phenols small amounts of *m*-chlorophenol but significant amounts of *m*-bromophenol. The formation of these meta isomers may proceed via a 3,4-dihydro 3,4-diol as suggested recently by Narita and Tezuka[14] in the hydroxylation of toluene (Scheme II). In addition to the Dorfman mechanism,[15] there is a dihydrodiol mechanism operating.

Our results show an increase in the percentage of meta isomer with increasing temperature. This is consistent with the mechanism in Scheme II. The unimolecular decomposition (the Dorfman mechanism) is favored at the lower steady-state concentrations, whereas the dihydrodiol mechanism, which involves a bimolecular disproportionation, is favored at the higher steady-state concentrations. In the chlorobenzene case the yield of *m*-chlorophenol is indeed very small, indicating that under our reaction conditions the Dorfman mechanism is predominant.

Another possible mechanism for the formation of *m*-bromophenol is via OH elimination and readdition (Scheme III).

Scheme II



This mechanism would also explain the increase in the percentage of *m*-bromophenol at higher temperature due to the greater fraction of hydroxybromocyclohexadienyl radicals undergoing dissociation to bromobenzene and OH radicals.

In the presence of oxygen the yields of chlorophenols and bromophenols increase dramatically both in the absence and presence of nitrobenzene, and the yield of nitrophenol decreases (Tables II and III). The rate of dissociation (eq 4, Scheme I) has to compete with the oxidation to chlorophenols and bromophenols (eq 5, Scheme I). The rate constants for oxidation by oxygen of the hydroxychlorocyclohexadienyl radical[16] ($k = 7.95 \times 10^6$ M^{-1} s^{-1}) and the hydroxybromocyclohexadienyl radical[16] ($k = 9.6 \times 10^6$ M^{-1} s^{-1}) are much less than the rate con-

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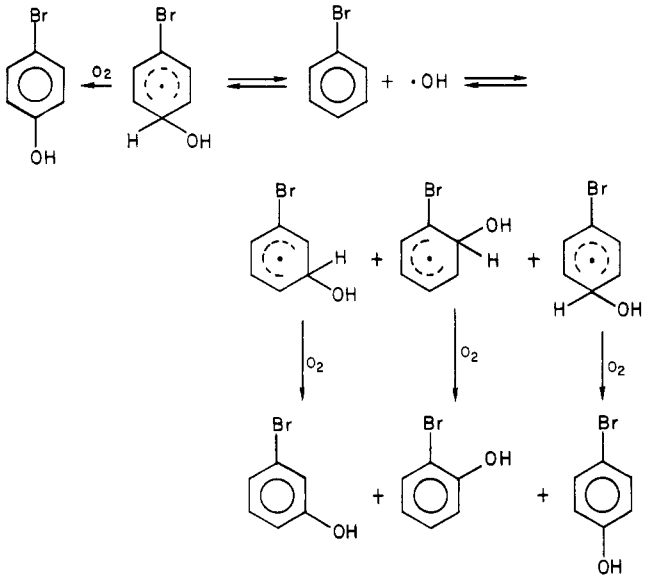
Scheme III



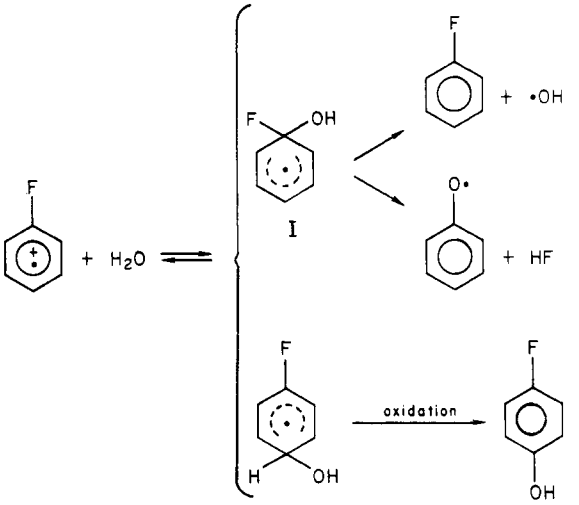
stants for oxidation of the unsubstituted hydroxycyclohexadienyl radical[16] ($k = 4.0 \times 10^8$ M^{-1} s^{-1}). The rate of oxidation by oxygen is therefore competing less efficiently with the dissociation in these experiments with chloro- and bromobenzene as compared to benzene. We obtain some nitrophenols even in presence of oxygen, whereas in our benzene experiments in the presence of oxygen no nitrophenols were formed.[2,3] In the presence of oxygen, more nitrophenols are formed in the bromobenzene experiments than in the chlorobenzene experiments. This is probably due to a greater k(dissociation) for the hydroxybromocyclohexadienyl radical.

A most interesting result is the formation of *m*-nitrophenol. In the bromobenzene experiments we obtain a nitrophenol isomer distribution of 53% ortho, 26% meta, and 21% para at 25 °C and 52% ortho, 24% meta, and 24% para at 80 °C, whereas in absence of oxygen only *o*- and *p*-nitrophenols are formed. The formation of *m*-nitrophenol in the presence of oxygen is not surprising in view of previous results on the radiation-induced hydroxylation of nitrobenzene.[17-19] These results showed an increase in *m*-nitrophenol in the presence of oxygen. We have shown that OH radicals attack nitrobenzene in a statistical manner, giving rise to (in presence of efficient oxidizing agents, like $K_3Fe(CN)_6$ a 40% ortho, 40% meta, and 20% para isomer distribution.[26] In the absence of oxidizing agents or with less efficient oxidizing agents, the meta adduct rearranges to the more stable ortho and para adducts[19] before being oxidized. The formation of *m*-nitrophenol in the bromobenzene and to a lesser extent in the chlorobenzene experiments is consistent with the formation of free OH radicals.

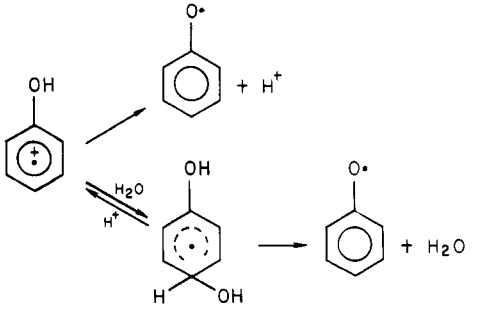
Among the monohalogenated benzenes only chloro- and bromobenzene radical cations give nitrophenols. We have studied the hydroxylation of fluorobenzene via its radical cation,[12] and we have found that nucleophilic addition of water takes place at the α and para positions in agreement with SCF-MO calculations (Scheme IV).

In the absence of effective oxidizing agents, we found that phenol was the main product. The ipso intermediate I has been observed by pulse radiolysis.[20] It was shown

Scheme IV



Scheme V



to be extremely short-lived, undergoing unimolecular decomposition to phenoxy radicals.[20]

The decomposition of the ipso intermediate may involve an $S_{ON}2$ reaction as was discussed by Alder.[21] It was pointed out by Eberson and Jonsson[22] that such a mechanism may be involved in the formation of phenol from fluorobenzene radical cation in aqueous solution:

$$[RF]^{+\cdot} + OH^- \rightarrow [RFOH]\cdot \rightarrow [ROH]^{+\cdot} + F^-$$

$$[ROH]^{+\cdot} + RF \rightarrow ROH + [RF]^{+\cdot}$$

In any case the fast decomposition of the ipso intermediate competes effectively with the slow dissociation to fluorobenzene and OH radicals. The results in Table I show that phenol is the main product both in the absence and presence of nitrobenzene and that only trace amounts of nitrophenols are formed.

Phenol radical cation reacts via elimination of a proton or via hydroxycyclohexadienyl radicals, which undergo acid-catalyzed dehydration to give phenoxy radicals[23] (Scheme V).

Analogous reactions have been observed with toluene radical cation.[11,12,24,25] If in the toluene radical cation the proton elimination pathway is blocked by substitution, as in *tert*-butylbenzene, the radical cation adds water to produce a hydroxy cyclohexadienyl radical, which can dissociate to *tert*-butylbenzene and OH radicals (see under Results).

In summary we can say that OH radicals are formed from aromatic radical cations under the following condi-

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tions: (1) the radical cation must add water to produce a hydroxycyclohexadienyl radical and (2) the hydroxycyclohexadienyl radical has no alternate pathways of decomposition.

Experimental Section

The experimental procedures have been described previously.[2,3] In the experiments at 80 °C, after 1 h about 20% of $S_2O_8^{2-}$ has decomposed, i.e., 4.5×10^{-4} mol, yielding, for example, in expt 6, Table II, 32×10^{-5} mol of phenols. The phenol, chlorophenols, and bromophenols were analyzed by gas chromatography using a 6-ft column of FFAP (5%) on Chromasorb W-AW-DMCS and a flow rate of 25 mL/min. This column was used at 220 °C for the analysis of *p*-chloro- and *p*-bromophenol (7.8 and 12.2 min, respectively) and at 180 °C for the analysis of *o*-chlorophenol, *o*-bromophenol, and phenol (4.5, 6.6, and 7.2 min. respectively). In the experiments with chlorobenzene and nitrobenzene, the *o*-chlorophenol appeared immediately after the big nitrobenzene peak when using the above column and conditions. We therefore used another column for these samples: 6 ft DEGS + 6 ft SF-96 (10% liquid phase on Chromosorb W-AW-DMCS) at 160 °C. Under these conditions the retention times were 5.0 min for *o*-chlorophenol, 5.5 min for nitrobenzene, and 7.8 min for phenol. The nitrophenols were analyzed after methylation with diazomethane on a 6 ft FFAP column at 200 °C as described.[26] The separation of the *m*- and *p*-chlorophenols and the *m*- and *p*-bromophenols was accomplished after silylation with BSA (Supelco, Inc.). The silylated derivatives could be separated on a 10-ft column of 5% SE-30 on 80/100 Supelcoport at 130 °C. Under these conditions the meta isomer appears before the para isomer.

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Registry No. Disodium persulfate, 7775-27-1; nitrobenzene, 98-95-3; hydroxy radical, 3352-57-6; fluorobenzene, 462-06-6; chlorobenzene, 108-90-7; bromobenzene, 108-86-1.

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Liquid Crystalline Solvents as Mechanistic Probes. 11. The Syn → Anti Thermal Isomerization Mechanism of Some Low-"Bipolarity" Azobenzenes[1]

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The effects of solvent order on the syn → anti isomerization rates of 15 azobenzenes have been investigated. The activation parameters determined in a cholesteric phase consisting of a 35/65 (w/w) mixture of cholesteryl chloride/cholesteryl nonanoate and in several other solvents are more consistent with an isomerization mechanism which proceeds via inversion (in plane) rather than rotation (out of plane). A correction of our previously reported data is given. The anomalous behavior of the isomerization mechanism of di-ortho-methylated azobenzenes is demonstrated by means of isokinetic plots.

The mechanism of the thermal syn → anti isomerization of azobenzene (1) has been investigated extensively for more than 40 years[2] and remains a subject of controversy. It is known to follow first-order kinetics which are slightly dependent upon solvent polarity in a wide variety of media[3] and phases: for instance, in the melt,[4] $E_a = 24.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = -5$ eu; in the vapor phase,[5] $E_a = 28$ kcal mol^{-1} and $\Delta S^{\ddagger} = +3$ eu. Unfortunately, none of these studies has been able to distinguish unambiguously between an inversional (in plane) motion and a rotational (out of plane) motion for the isomerization (Figure 1).

Theoretical calculations favoring the inversional process have been reported.[6] However, no treatment to date has included a wide selection of C–N rotamers in the transition states, and, of those which reproduce the experimental syn → anti isomer energy difference (9.9 kcal mol^{-1} [7]), none has been extended to calculate activation energies for isomerization.[8]

Recently, the isomerization of azobenzene has been reexamined by using some novel mechanistic tools. For instance, Rau and Lüddecke[9] measured the activation energy for syn,anti → anti,anti isomerization in a cyclic bichromophoric azobenzene in which a rotational mechanism can occur only with great difficulty. The fact that the observed activation energy is smaller than that found for syn → anti isomerization of **1** in the same solvent provides evidence for the inversional mechanism. Shinkai

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