Reaction of Benzene Radical Cation with Water. Evidence for the Reversibility of OH Radical Addition to Benzene

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Abstract: The thermal decomposition of $Na_2S_2O_8$ at 80 °C in aqueous solutions of benzene and nitrobenzene gives phenol, biphenyl, and *o*- and *p*-nitrophenol in high yield. In the absence of benzene or if benzene is replaced by toluene or anisole no nitrophenols are formed under otherwise identical conditions. This indicates a direct involvement of the benzene radical cation in the hydroxylation of nitrobenzene. The benzene radical cation reacts with water to give hydroxycyclohexadienyl radical, which in turn can dissociate to benzene and OH radicals. The effect of oxygen, Cu^{2+}, pH, and benzene concentration on the product yields has been investigated.

In a series of previous publications[1-5] we have discussed in detail the factors influencing the isomer distribution in the homolytic hydroxylation of monosubstituted aromatic compounds. These reactions are summarized in Scheme I.

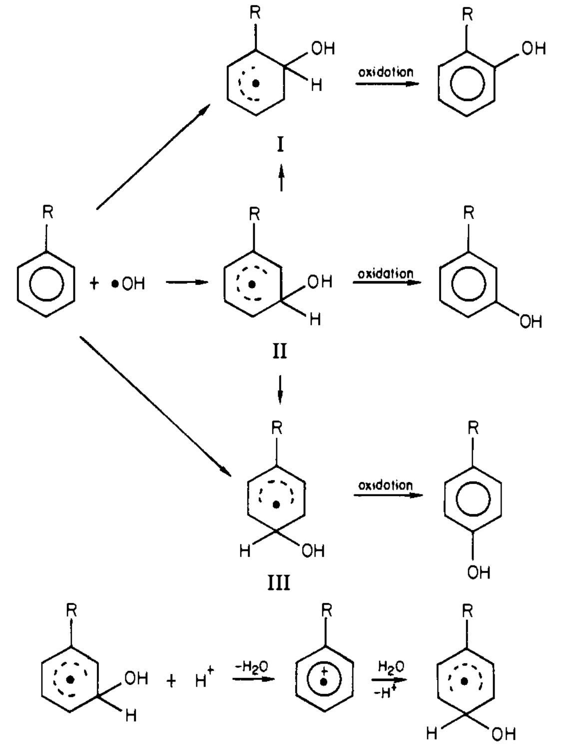
From the work of Walling and Camaioni[6] as well as from our own results[4,5] it is evident that in some cases (toluene, fluorobenzene) the isomerization of II → I and III proceeds via an acid-catalyzed reversible water elimination. In other cases (nitrobenezene, benzonitrile, anisole) where this reversible water elimination does not occur[4,7,8] we suggested a radical rearrangement to form the more stable ortho and para adducts.[1,2,4] We have now obtained evidence for the reversibility of OH radical addition to benzene, which lends additional support to a free-radical rearrangement (II → I and III) in the hydroxylation of some monosubstituted aromatics.

Results and Discussion

We have studied the thermal decomposition of $S_2O_8^{2-}$ in dilute aqueous solutions saturated with benzene and nitrobenzene. The results are summarized in Tables I and II. In the absence of benzene no nitrophenol is formed under otherwise identical conditions. The results with nitrobenzene in oxygenated solutions (Table I, experiment 8) clearly demonstrate the absence of hydroxynitrocyclohexadienyl radicals, since it is well established that oxygen oxidizes these radicals to nitrophenols.[9] In all cases in which both benzene and nitrobenzene were present only *o*- and *p*-nitrophenol were observed in a ratio of about 2:1. From the foregoing it follows that the hydroxycyclohexadienyl radical is directly involved in the hydroxylation of nitrobenzene. We propose the mechanism in Scheme II.

The formation of aromatic radical cations by $SO_4^{-}\cdot$ is now firmly established through the work of a number of investigators.[8,10-15]

Scheme I



On the basis of the known rate constants[15] for the reaction of benzene (3×10^9 M^{-1} s^{-1}) and nitrobenzene ($\leq 10^6$ M^{-1} s^{-1}) with $SO_4^{-}\cdot$ we can rule out the formation of nitrophenols via the nitrobenzene radical cation. In most experiments (experiments 1-5, Table II) in which benzene was present on the basis of these rate constants practically 100% of the SO_4^- radicals must react initially with benzene. Therefore, the nitrophenols produced cannot be due to any reaction involving nitrobenzene + $SO_4^{-}\cdot$. It has been established by pulse radiolysis that benzene radical cation reacts rapidly (≤ 0.1 μs) with water to produce the hydroxycyclohexadienyl radical,[15] which we now propose can in turn dissociate to benzene and OH radical. Calculations by Jackson[16] have shown that homolytic addition to benzene is about 11 kcal less exothermic than addition to ethylene. Since the addition of OH radical to ethylene is exothermic by 33 kcal,[17] the addition to benzene must be exothermic by about 22 kcal/mol. Assuming a rate constant

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[17] Calculated from *D*(R-OH) for ethanol (-91 kcal) and the π bond energy for ethylene (58 kcal).

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Table I[a]

				products, mol × 10^5			
						nitrophenols	
expt no.	reagents[1]	temp, °C	time[2]	phenol	biphenyl	ortho	para
1	PhH	80	40 min	2.5	9.3		
2	PhH, $PhNO_2$	80	40 min	15.6	5.3	11.7	5.6
3	PhH	80	1 hr	4.5	14.3		
4	PhH, $PhNO_2$	80	1 hr	28.0	6.2	17.5	8.5
5	$PhNO_2$	80	40 min				
6	$PhNO_2$	80	1 hr				
7	$PhNO_2$	80	2 hrs				
8	$PhNO_2$ (oxygen saturated)	80	40 min				

[a] In all experiments the following concentrations were used: 2×10^{-2} mol of PhH, 4.7×10^{-3} mol of $PhNO_2$. All experiments contained 2.5×10^{-3} mol of $Na_2S_2O_8$ in 500 mL of triple distilled water. The pH of these solutions was about 3.0 in all experiments (except no. 8). The solutions were deoxygenated by bubbling Argon through the solution for about 30 min. In experiment 8 the solution was saturated with oxygen for 30 min.

Table II[a]

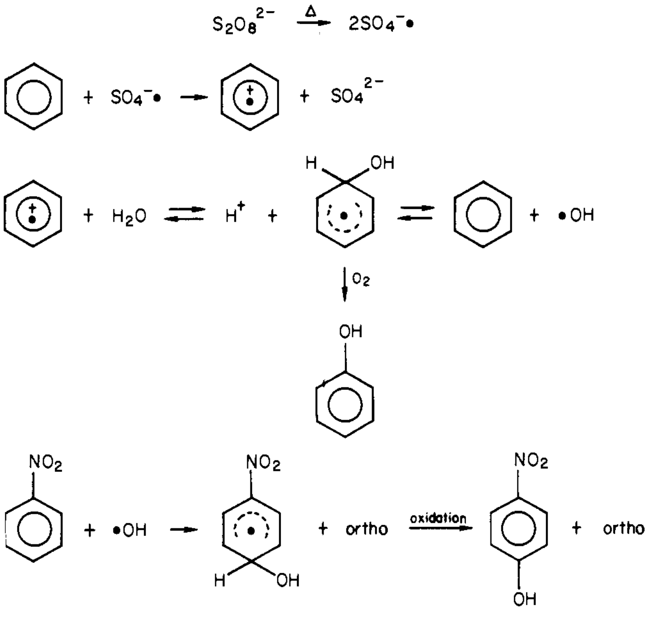
		products, mol × 10^5				
				nitrophenols		
expt no.	[PhH], mol	phenol	biphenyl	ortho	para	nitrophenols/ phenol
1	2.0×10^{-2}	15.6	5.3	11.7	5.6	1.11
2	9.0×10^{-3}	14.6	2.9	16.8	8.7	1.75
3	4.5×10^{-3}	10.8	1.4	19.5	10.0	2.76
4	2.25×10^{-3}	7.6	0.6	20.3	10.5	4.06
5	6.25×10^{-4}	trace	trace	15.7	7.6	
6	3.12×10^{-4}	trace	trace	11.2	6.3	
7	1.25×10^{-4}			3.6	3.2	
8	6.25×10^{-5}			1.3	1.5	
9	2.0×10^{-2} (pH 1,6)	6.2	0.9	3.5	1.6	0.82
10	9.0×10^{-3} (not deoxygenated)	24.5	1.6	13.0	5.7	0.76
11	9.0×10^{-3} (O_2 sat.)	48.0				
12	4.5×10^{-3} (O_2 sat.)	39.5				
13	2.25×10^{-3} (O_2 sat.)	30.0				
14	6.25×10^{-4} (O_2 sat.)	6.4				
15	4.5×10^{-3} ($CuSO_4$, 10^{-4})	44.0		12.5	5.7	
16	4.5×10^{-3} ($CuSO_4$, 9×10^{-4})	60.0		1.6	0.8	

[a] All experiments were carried out by heating 500-mL solutions at 80 °C for 40 min. and contained in addition to benzene 4.7×10^{-3} mol of nitrobenzene and 2.5×10^{-3} mol of $Na_2S_2O_8$. Experiments 1-9 were deoxygenated prior to heating. In experiment 9 the pH was adjusted by adding 1.38 mL of concentrated H_2SO_4 prior to heating. In experiment 10 no Argon was bubbled through the solution. In experiments 11-14 oxygen was bubbled through the solution for 30 min.

of 4.5×10^8 M^{-1} s^{-1} for the bimolecular disproportionation and dimerization of the hydroxycyclohexadienyl radicals as determined by pulse radiolysis by Cercek,[18] we can estimate that under our conditions (half-life of $S_2O_8^{2-}$ about 140 min) these radicals have a life-time of about 0.074 s. If we further assume a large *A* factor (10^{15}–10^{16}) for the unimolecular decomposition, this permits an activation energy of 22.8–24.4 kcal/mol. A large *A* factor of 4×10^{15} has been determined for the unimolecular decomposition of the cyclohexadienyl radical.[19] Our proposed mechanism therefore appears reasonable on energetic grounds. One may envisage another low-energy pathway in which the OH radical is transferred from the hydroxycyclohexadienyl radical to nitrobenzene without ever being completely free. However, since the mechanism proposed above appears energetically feasible, we tend to favor this scheme.

Some of the hydroxycyclohexadienyl radicals are also oxidized by nitrobenzene to phenol. This can be seen by comparing experiments 1 and 2 in Table I. The oxidation of cyclohexadienyl type radicals by nitrobenzene has been reported previously in the homolytic phenylation of benzene.[20] This oxidation to phenol takes place rapidly only at elevated temperatures.[21]

Scheme II



Only *o*- and *p*-nitrophenols are formed in agreement with the greater stability of the *o*- and *p*-hydroxynitrocyclohexadienyl radicals.[1] Under our reaction conditions of low concentration and

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elevated temperatures the hydroxynitrocyclohexadienyl radicals have sufficient time to equilibrate ($PhNO_2 + OH \rightleftarrows HO—Ph—NO_2$) before being oxidized to the nitrophenols. The results in Table II show that decreasing the concentration of benzene increases the ratio of nitrophenols/phenol as expected for a reaction in which benzene and nitrobenzene compete for the hydroxylating species.

Since the elimination of OH radical from the hydroxycyclohexadienyl radical is a high activation energy process, this reaction cannot be observed at 25 °C[22] or in the presence of oxidizing agents. Oxygen[23] and cupric ion[24] oxidize hydroxycyclohexadienyl radicals to phenol. Some results in the presence of oxygen and Cu^{2+} are shown in Table II (experiments 10–16). Oxidation competes with the dissociation to benzene and OH radicals, and thus decreases the yield of nitrophenols. At low oxygen concentration (experiment 10) nitrophenol is still formed, but if the solution is saturated with oxygen (experiments 11–14) phenol is the only product. If we compare experiments 2 and 10, we can see that the total product yield is about the same, but in experiment 10 we obtain more phenol and less nitrophenol compared to that found in experiment 2. Cu^{2+} shows a similar effect (compare experiments 3, 15, and 16).

If benzene is replaced by toluene no nitrophenols are formed. The only products are benzaldehyde and benzyl alcohol.[25] This observation also agrees with our proposed mechanism. Toluene radical cation instead of adding water will preferentially eliminate a proton to give benzyl radicals, which in turn are oxidized to benzaldehyde and benzyl alcohol.[5,6,26] We therefore produce no OH radicals and no nitrophenols.

If in experiment 2 (Table I) benzene was replaced by 5×10^{-3} mol of anisole, we again do not observe any formation of nitrophenols. Under these conditions 100% of $SO_4^{-}\cdot$ reacts initially with anisole.[15] It is well known that anisole radical cation does not add water,[7,8] and therefore according to our scheme does not produce OH radicals.

Other indirect evidence for the reversibility of OH radical addition to aromatics can be found in the literature. Balakrishnan and Reddy[27] have studied the radiation-induced hydroxylation of naphthalene and found with increasing temperature (27–94 °C) a remarkable decrease in β-hydroxylation. Although the authors did not discuss the mechanistic aspects of this change in isomer ratio, their results can be explained by a reversible addition and formation of the more stable α intermediate as required by theory.[28]

Experimental Section

All experiments were carried out with 2.5×10^{-3} mol of $Na_2S_2O_8$ in 500 mL of triple distilled water. The solutions were deoxygenated by bubbling Argon through the solution for about 30 min with occasional shaking. The benzene and/or nitrobenzene was injected through a rubber septum and the solution was vigorously shaken and heated in a water bath at 80 °C. The reaction was stopped by cooling in ice. The mixture was then extracted once with 200 mL of ether and three times with 100 mL of ether. The combined ether extracts were dried over Na_2SO_4 and concentrated to 10 mL and then analyzed by gas chromatography as described previously.[4,5] The nitrophenols were analyzed after methylation with diazomethane.[2] Most experiments were repeated several times and the results were found to be reporducible within ±10% in the worst case. Most experiments were reproducible with ±5%. In one experiment (no. 4, Table I) the disappearance of $S_2O_8^{2-}$ was determined iodometrically,[29] and it was found that 28% had reacted. In this experiment we have therefore obtained an almost quantitative product yield.

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Thermolysis of α-Azido Sulfides, Sulfoxides, and Sulfones: Dependence of Mechanism on Oxidation State of Sulfur

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Abstract: Thermolyses of α-azidobenzyl phenyl sulfide (**1**), sulfoxide (**3**), and sulfone (**2**) proceed at markedly different rates. Sulfone **2** requires the highest temperature (>150 °C), whereas sulfide **1** loses nitrogen at 120 °C with neighboring group participation by the sulfur atom to produce *N*-benzylidenebenzenesulfenamide **4** in 75% yield. Sulfoxide **3** readily decomposes at 70 °C through a radical-pair intermediate, which gives rise to a CIDNP effect in the reaction products. Kinetic data are presented supporting the suggested reaction mechanisms.

The thermolysis of azides with loss of nitrogen is one of the most characteristic and useful reactions of organic azides.[1] These reactions often involve nitrene intermediates[1] though there are a number of notable exceptions where apparent neighboring-group participation by adjacent nucleophilic groups obviates the normal nitrene intermediate. These reactions are characterized by their occurrence at significantly lower temperatures and, where the data have been determined, by having significantly negative entropies of activation.[2]

For some time, we have been interested in the chemistry of organic sulfur compounds which possess halogen atoms on the carbon bearing the sulfur functionality.[3] Since azides are

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