Radiation-Induced Homolytic Aromatic Substitution. IV. Effect of Metal Ions on the Hydroxylation of Nitrobenzene

Manfred K. Eberhardt

Puerto Rico Nuclear Center, Caparra Heights Station, San Juan, Puerto Rico 00935 *(Received March 28, 1975)*

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The effect of chromium(VI), iron(III), iron(II), and copper(II) compounds on the radiation-induced hydroxylation of nitrobenzene has been investigated. $K_2Cr_2O_7$ in unbuffered solution and $K_3Fe(CN)_6$ in acidic (pH 1.4) solution gave a high conversion of hydroxyl radicals to nitrophenols with a close to statistical isomer distribution. The isomer distribution obtained with $K_3Fe(CN)_6$ in acidic solution did not change with concentration (5×10^{-4} to 5×10^{-2} M). On the other hand with $K_2Cr_2O_7$ the G(meta) increased with concentration (5×10^{-4} to 5×10^{-3} M) approaching a close to statistical distribution at the higher concentration. In unbuffered solution $K_3Fe(CN)_6$ produced mainly *m*-nitrophenol. We suggest that this is due to a selective oxidation of the *m*-hydroxynitrocyclohexadienyl radical, and to a selective reduction of the *o*- and *p*-hydroxynitrocyclohexadienyl radicals by $Fe(CN)_6^{4-}$. Contrary to the results with $K_2Cr_2O_7$ and $K_3Fe(CN)_6$, the Fe^{3+} salts ($FeNH_4(SO_4)_2$, $Fe(ClO_4)_3$, and $Fe(NO_3)_3$) at low concentration (5×10^{-4} M) gave almost exclusively ortho and para hydroxylation in high yield. The mechanism of these oxidations is discussed. Cu^{2+} (5×10^{-4} M) does not oxidize the intermediate hydroxycyclohexadienyl radicals. In all cases ($CuSO_4$, $CuCl_2$, $Cu(ClO_4)_2$, and $Cu(OCOCH_3)_2$) only trace amounts of nitrophenols with the para isomer dominant (G(para) ~ 0.1) were obtained. Depending on the metal ion, concentration, and pH, one may produce either *m*-nitrophenol (100%) or *o*- and *p*-nitrophenol (97.4%) or a statistical isomer distribution.

Introduction

In a previous publication[2a] we have reported on the radiation-induced hydroxylation of nitrobenzene, chlorobenzene, and toluene. In absence of oxygen the yields of the substituted phenols were much smaller than $G(\cdot OH)$ due to competing side reactions, such as disproportionation, dimerization, recombination of the ·OH radical adduct with the H· atom adduct,[2b] and in the case of toluene elimination of water.[3] Oxygen has been frequently used to increase the yields in homolytic aromatic substitution.[2a,4,5] Oxygen considerably increases the yields of nitrophenols, chlorophenols, and cresols, but is still much lower than $G(\cdot OH)$. In the hydroxylation of benzene Baxendale and Smithies[6] have been able to convert ·OH radicals quantitatively to phenol in presence of a mixture of $FeNH_4(SO_4)_2$ and $CuSO_4$. Volkert and Schulte-Frohlinde[7] in their study of the hydroxylation of benzoic acid in presence of N_2O used $K_3Fe(CN)_6$ to convert all the ·OH radicals to hydroxybenzoic acids. Most recently Bhatia and Schuler[8] have studied the effect of a variety of metal salts on the hydroxylation of benzene in N_2O-saturated aqueous solutions, and observed in some cases a G(phenol) = 6.0. In order to obtain more reliable information about the initial position of ·OH radical attack on substituted benzenes it is of course desirable to convert all the ·OH adducts to the corresponding phenols. No study on the reduction of substituted hydroxycyclohexadienyl radicals has been reported. In the present work we have studied the effects of chromium(VI), iron(III), iron(II), and copper(II) compounds and oxygen on the hydroxylation of nitrobenzene.

Experimental Section

Materials. All solutions were prepared using water which was triple distilled from an all glass still. Then it was further distilled over alkaline permanganate, acidic dichromate, and one final distillation. Nitrobenzene was reagent grade and was redistilled. All metal salts were of reagent grade quality. The aqueous solution were deoxygenated by bubbling argon through the solution as described previously.[2a]

Irradiations. Irradiations were carried out with a ^{60}Co source at a dose rate of 2.56×10^{16} eV/g min and a total dose of 1.54×10^{18} eV/g (determined by Fricke dosimetry with $G(Fe^{3+}) = 15.5$). The dosimetry was carried out by using the same bottles and volume as the irradiated solutions.

Analytical Procedure. Immediately after the irradiation the pH of the solution (1 l.) was adjusted to about 4 and then extracted once with 200 ml of ether and four times with 100 ml of ether. The ether extract was dried over 80 g of Na_2SO_4 for about 24 hr, and was then concentrated to about 20–30 ml. To this concentrate was added 20 ml of a diazomethane solution (prepared from Diazald, Aldrich Chemical Co.) and left standing for 2 days. This procedure converted all the nitrophenols quantitatively to the corresponding methoxy derivatives. Then the solution was concentrated to 10 ml and analyzed by vapor phase chromatography using a hydrogen flame detector. The column was a 6-ft DEGS (diethyleneglycol succinate 5% liquid phase on Chromosorb W-AW-DMCS (100–120 mesh)) column at 170° and a flow of about 25 ml of He/min. The isomeric nitroanisoles appeared in the following sequence: *m*-nitroanisole (5.0 min), *o*-nitroanisole (7.9 min), and *p*-nitroanisole (8.9 min). Standard aqueous nitrophenol solutions were prepared containing amounts of nitrophenols which were very close to the amounts present in the irradiated solutions and worked up in the same way. In this way a very accurate determination of the G values was possible. All experiments were carried out in duplicate and triplicate and were found to be reproducible within the limits of the ana-

TABLE I: Nitrophenol Yields in the Radiolysis of Aqueous Nitrobenzene Solutions[a]

Expt no.	Conditions	G(ortho)	G(meta)	G(para)	G(total)	% ortho	% meta	% para
1	$K_2Cr_2O_7$ 5 × 10^{-4} M	1.50	0.98	0.63	3.11	48.2	31.5	20.3
2	$K_2Cr_2O_7$ 5 × 10^{-3} M	1.50	1.29	0.60	3.39	44.2	38.1	17.7
3	$K_2Cr_2O_7$ 5 × 10^{-4} M pH 1.4	1.00	0.53	0.48	2.01	49.8	26.4	23.9
4	$K_3Fe(CN)_6$ 5× 10^{-4} M	0.15	0.95	0.18	1.28	11.7	74.2	14.1
5	$K_3Fe(CN)_6$ 5 × 10^{-4} M	0.12	1.02	0.20	1.34	9.0	76.1	14.9
6	$K_3Fe(CN)_6$ 5 × 10^{-3} M	0.15	1.05	0.22	1.42	10.6	73.9	15.5
7	$K_3Fe(CN)_6$ 5 × 10^{-2} M	0.35	1.13	0.33	1.81	19.3	62.4	18.2
8	$K_3Fe(CN)_6$ 5 × 10^{-4} M + $K_4Fe(CN)_6$ 5 × 10^{-4} M	0	0.90	0	0.90	0	100	0
9	$K_3Fe(CN)_6$ 5 × 10^{-4} M pH 1.4	1.14	0.98	0.50	2.62	43.5	37.4	19.1
10	$K_3Fe(CN)_6$ 10^{-3} M pH 1.4	1.14	0.98	0.47	2.59	44.0	37.8	18.2
11	$K_3Fe(CN)_6$ 2 × 10^{-3} M pH 1.4	1.12	1.05	0.50	2.67	41.9	39.3	18.7
12	$K_3Fe(CN)_6$ 5 × 10^{-3} M pH 1.4	1.10	1.08	0.50	2.67	41.9	39.3	18.7
13	$K_3Fe(CN)_6$ 10^{-2} M pH 1.4	1.15	1.13	0.52	2.80	41.1	40.4	18.6
14	$K_3Fe(CN)_6$ 5 × 10^{-4} M + $K_4Fe(CN)_6$ 5 × 10^{-4} M pH 1.4	0.62	1.02	0.34	1.98	31.3	51.5	17.2
15	$FeNH_4(SO_4)_2$ 5 × 10^{-4} M	1.44	0.08	0.81	2.33	61.8	3.4	34.8
16	$FeNH_4(SO_4)_2$ 5 × 10^{-4} M + $Fe(NH_4)_2(SO_4)_2$ 5 × 10^{-4} M	0.47	0.08	0.70	1.25	37.6	6.4	56.0
17	$Fe(ClO_4)_3$ 5 × 10^{-4} M	1.30	0.08	0.77	2.15	60.5	3.7	35.8
18	$Fe(ClO_4)_3$ 5 × 10^{-3} M	1.46	0.24	0.80	2.50	58.4	9.6	32.0
19	$Fe(ClO_4)_3$ 5 × 10^{-2} M	1.60	0.44	0.82	2.86	55.9	15.4	28.7
20	$Fe(ClO_4)_3$ 5 × 10^{-4} M + $HClO_4$ 5 × 10^{-2} M	1.97	0.08	1.02	3.07	64.1	2.6	33.3
21	$Fe(NO_3)_3$ 5 × 10^{-4} M	1.44	0.08	0.85	2.37	60.8	3.4	33.8
22	$Fe(NO_3)_3$ 5 × 10^{-3} M	1.44	0.26	0.75	2.45	58.8	10.6	30.6
23	$Fe(NO_3)_3$ 5 × 10^{-2} M	1.11	0.25	0.55	1.91	58.1	13.1	28.8
24	$Fe(NO_3)_3$ 5 × 10^{-4} M + O_2 10^{-3} M	1.14	0.63	0.59	2.36	48.3	26.7	25.0
25	No additives	0.18	0.05	0.36	0.59	30.5	8.5	61.0

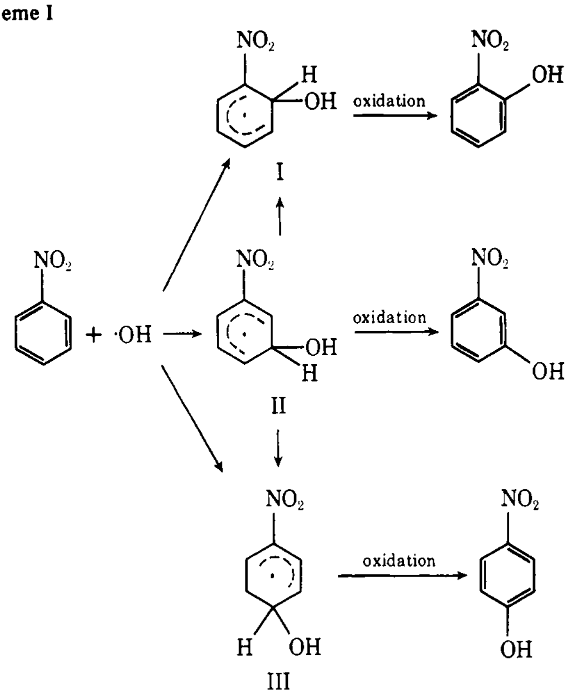
[a] All solutions were deoxygenated (except experiment 24) solutions (5 × 10^{-3} M nitrobenzene) irradiated at a dose rate of 2.56 × 10^{16} eV/g min and a total dose of 1.54 × 10^{18} eV/g. All solutions were unbuffered. Experiments at pH 1.4 contained H_2SO_4.

lytical technique (±5%). The smaller G values (<0.5) are somewhat less accurate (±8%).

Results and Discussion

The results are shown in Table I. The $G(\cdot OH)$ values at pH 7 reported in the literature vary over a wide range (2.0–3.2).[9] More recently Bielski and Allen[10] have determined $G(\cdot OH) = 2.74 \pm 0.08$ at pH 7. The results in Table I show that, under certain conditions of concentration and pH, excellent conversions of the ·OH radicals to nitrophenols are obtained. With 5 × 10^{-3} M $K_2Cr_2O_7$ in unbuffered solution we observe a G(total nitrophenols) of 3.29. The high G(total nitrophenols) may be partly due to a reaction between the reduced metal ion and H_2O_2, which would increase the $G(\cdot OH)$ by as much as the molecular peroxide yield (ca. 0.7). Evidence for this type of additional hydroxylation has also been obtained by Bhatia and Schuler[8] in the hydroxylation of benzene. A G(phenol) of 3.2 was reported by Baxendale and Smithies[6] in presence of 5 × 10^{-4} M Fe^3 + 2 × 10^{-3} M Cu^{2+}. The drastic difference in the isomer distribution obtained with $K_2Cr_2O_7$ and $K_3Fe(CN)_6$ on one hand and with the Fe^{3+} salts on the other hand is apparent. With $K_2Cr_2O_7$ and $K_3Fe(CN)_6$ we obtain much more meta substitution than with the Fe^{3+} salts, which give mainly ortho–para substitution. In order to discuss this great variation in isomer distribution we suggest the mechanism outlined in Scheme I. The ·OH radical adducts (I–III) can be oxidized by some metal ions to the corresponding nitrophenols. This oxidation will compete with the 1,2 hydroxyl radical shift II → I and II → III, and also with the reduction by the reduced metal ion. With increasing $Fe(ClO_4)_3$ and $Fe(NO_3)_3$ concentration the percentage of m-nitrophenol increases as expected for this competition between oxidation and rearrangement. Evidence for a 1,2 hydroxyl radical shift has been presented previously in the hydroxylation of benzoic acid[7] and anisole.[11] SCF–MO calculations of OH radical adducts of nitrobenzene, chlorobenzene, and toluene have shown that in all cases the ortho and para adducts have the lowest energies.[2a] For the mechanism of the rearrangements II → I and II → III several possibilities exist. A reversible addition possibly involving a π complex has been suggested by Volkert and Schulte-Frohlinde.[7] Recently Walling and Johnson[12] in the hydroxylation of toluene with Fenton's reagents have proposed a reversible dehydration, which could lead to isomerization. In the case of the hydroxynitrocyclohexadienyl radicals however this possible mechanism can be excluded since results of Schevchuk and Vysotskaya[13] on the hydroxylation

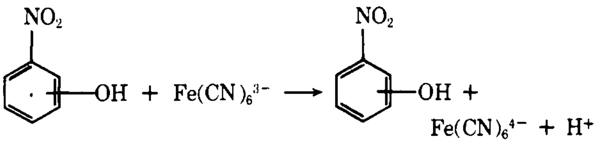
Scheme I



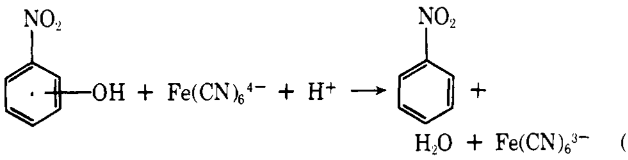
of nitrobenzene with Fenton's reagent have shown that the oxygen in the nitrophenols is solely derived from H_2O_2 and not from the water.

The anion has no effect on the isomer distribution (see experiments 15, 17, and 21). This was also observed in the oxidation of *n*-butyl radicals in water by Cu^{2+} salts,[14] and is due to the extensive hydrolysis of the salts to solvated metal ions. With $Fe(ClO_4)_3$ we find an increase and with $Fe(NO_3)_3$ we find a decrease in the total nitrophenol yield with increasing concentration. At higher NO_3^- concentration $NO_2\cdot$ is produced (through e_{aq}^- scavenging by NO_3^-) which can compete with the Fe^{3+} for the intermediate hydroxycyclohexadienyl radicals.[15] $Fe(ClO_4)_3$ shows a considerable pH effect. At 5×10^{-4} *M* $Fe(ClO_4)_3$ and 5×10^{-2} *M* $HClO_4$ we obtain almost exclusively and in quantitative yield *o*- and *p*-nitrophenol (experiment 20).

The oxidations with $K_3Fe(CN)_6$ are pH dependent. The reduction potential of $Fe(CN)_6^{3-}$ changes from +0.69 eV in 1 *N* H_2SO_4 to +0.46 eV in 0.01 *N* NaOH.[16] The oxidation with $K_3Fe(CN)_6$ in neutral solution produced mainly *m*-nitrophenol (74%) with the same *G* value as in acidic solution, where we also obtain large amounts of *o*- and *p*-nitrophenol. This indicates a selective oxidation of the *m*-hydroxynitrocyclohexadienyl radical in neutral solution. According to SCF-MO calculations[2a] (CNDO and INDO) the *m*-hydroxynitrocyclohexadienyl radical has the highest lying SOMO (singly occupied molecular orbital) of the three isomers and is, therefore, the one which is most easily oxidized. The fact that with 5×10^{-4} *M* $K_3Fe(CN)_6$ in neutral solution we observed less *o*- and *p*-nitrophenol than in absence of $K_3Fe(CN)_6$[2a] made us suspect a selective reduction of the *o*- and *p*-hydroxynitrocyclohexadienyl radicals by $Fe(CN)_6^{4-}$ which is formed during the course of the irradiation. We have to consider the following two reactions:



(1)



(2)

We have studied the effect of $K_4Fe(CN)_6$ (experiment 8), and observed a complete disappearance of *o*- and *p*-nitrophenol, while the *m*-nitrophenol changes very little. The small decrease in *G*(meta) is due to the competition between nitrobenzene and $Fe(CN)_6^{4-}$ for OH radicals. On the basis of the known rate constants for these reactions (4.7×10^9 and 9.3×10^9 M^{-1} sec^{-1}, respectively)[17] one would expect a decrease of 20%. The selective reduction of the *o*- and *p*-hydroxynitrocyclohexadienyl radicals is also evident from the results in acidic solutions (experiment 14). In presence of $Fe(CN)_6^{4-}$ *G*(meta) does not change, but *G*(ortho) and *G*(para) decrease considerably. In neutral solution we observe with increasing $K_3Fe(CN)_6$ concentration an increase in *G*(ortho) and *G*(para) (experiments 4–7) in agreement with the two competing reactions (reaction 1 and 2). A reduction of the *o*- and *p*-hydroxynitrocyclohexadienyl radicals was also observed with $Fe(NH_4)_2(SO_4)_2$ (experiment 16).

With $K_3Fe(CN)_6$ at low pH we obtain a statistical isomer distribution which is independent of concentration. Accepting the mechanism outlined in Scheme I we can conclude that the rate of oxidation with $K_3Fe(CN)_6$ at low pH is very much faster than the rate of oxidation with Fe^{3+}.

Another possible explanation for the big difference between the $K_3Fe(CN)_6$ experiments and the Fe^{3+} experiments is a different oxidation mechanism. The oxidation of radicals by Fe^{3+} has been discussed by Walling and coworkers,[18] who suggested a reversible electron transfer process:

$$R\cdot + Fe^{3+} \rightleftharpoons R^+ + Fe^{2+}$$

The equilibrium is determined by the stability of the carbonium ion. In our case of three isomeric hydroxynitrocyclohexadienyl radicals we expect to obtain resonance stabilized carbonium ions, which can undergo a 1,2 hydroxide anion shift to give mainly *o*- and *p*-nitrophenol. In a study on the oxidation of hydroxyl radical–anisole adducts Norman and coworkers[11] have concluded that in the oxidation with metal ions the loss of a proton is synchronous with the electron transfer. They were led to that conclusion because in the hydroxylation of *p*-deuterioanisole with Fenton's reagent they only observed a small amount of a hydride shift (the NIH shift).[19] A 1,2 hydroxide anion shift, therefore, appears unlikely. Furthermore the increase in *m*-nitrophenol with increasing concentration of $Fe(ClO_4)_3$ or $Fe(NO_3)_3$ cannot be explained by a 1,2 hydroxide anion shift, but is indicative of competition between oxidation and rearrangement.

The preferential oxidation of the meta adduct by $Fe(CN)_6^{3-}$ and the preferential reduction of the ortho and para adducts by $Fe(CN)_6^{4-}$ is in agreement with results of Walling and coworkers.[18] They find that α-hydroxyalkyl radicals are oxidized by Fe^{3+}, while radicals with strong electron-withdrawing groups in the α position are instead reduced by Fe^{2+}. The *o*- and *p*-hydroxynitrocyclohexadienyl radicals have in one of their resonance forms the NO_2 group α to the radical site. We, therefore, suggest that the mechanisms of oxidation by $K_3Fe(CN)_6$ and Fe^{3+} are the same. The only difference between these two oxidizing metal salts is the much faster rate of oxidation by $K_3Fe(CN)_6$.

An interesting result is obtained with $Fe(NO_3)_3$ in oxygenated solution (experiment 24). Compared with the deoxygenated solution (experiment 21) *G*(meta) increases at the expense of *G*(ortho) and *G*(para), but *G*(total nitrophenols) remains the same. From this observation we conclude that k(oxidation with O_2)[20] = $2.5 \times 10^6\ M^{-1}\ \text{sec}^{-1} >$ k(oxidation with Fe^{3+}). The isomer distribution in oxygenated $Fe(NO_3)_3$ solution is almost identical with the one obtained in oxygenated nitrobenzene solutions in absence of $Fe(NO_3)_3$,[2a] but *G*(total nitrophenols) is higher (2.36 vs. 1.69[2a] or 1.75[21]).

The oxidation with $K_2Cr_2O_7$ has been investigated by Matthews and Sangster,[21] who obtained high conversions of the OH radicals to nitrophenols. We also find large *G*(nitrophenols) and we find in addition a considerable pH effect. At low pH the *G* values are lower than at neutral pH, probably due to further oxidation of the nitrophenols. Matthews and Sangster have suggested that all the hydroxynitrocyclohexadienyl radicals are oxidized to the corresponding nitrophenols. This, however, appears to be the case only at the higher $K_2Cr_2O_7$ concentration where we find a close to statistical isomer distribution.

Cu^{2+} salts ($CuSO_4$, $CuCl_2$, $Cu(ClO_4)_2$, and $Cu(OCOCH_3)_2$) at concentrations of $5 \times 10^{-4}\ M$ did not oxidize the hydroxynitrocyclohexadienyl radicals. At this concentration the reaction $Cu^{2+} + OH\cdot \rightarrow Cu(III) + OH^-$ ($k = 3.5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$)[17] will be insignificant compared to the reaction of $\cdot OH$ radicals with nitrobenzene ($k = 4.7 \times 10^9\ M^{-1}\ \text{sec}^{-1}$).[20] In all cases, only trace amounts of nitrophenols with the para isomer dominant ($G \sim 0.1$) were obtained. The oxidation of radicals with Cu^{2+} has been extensively investigated by Kochi and coworkers,[14] who have shown that the oxidation proceeds via an organocopper intermediate. Oxidation by Fe^{3+} proceeds by a different mechanism.[18] Cu^{2+} is known to oxidize the hydroxycyclohexadienyl radical[6,8] and hydroxymethylcyclohexadienyl radicals[22] to the corresponding phenols, but these radicals have much higher lying SOMO energy levels[2a] and have, therefore, lower oxidation potentials. The reduction potential of Cu^{2+} (+0.158 eV) is lower than that of Fe^{3+} (+0.770 eV). The oxidation with metal ions is competing with other radical termination processes. The reduction potential of the metal ion is, however, not the only factor which determines the rate of oxidation, since Ag^+ (+0.7996 eV) which has a higher reduction potential than Fe^{3+} or Cu^{2+} was found not to oxidize the hydroxycyclohexadienyl radical[8] whereas Fe^{3+} and Cu^{2+} did oxidize this intermediate.

The high yield of nitrophenols again confirms previous conclusions[20,23] that the $\cdot OH$ radicals attack at the ring and not, or only to an insignificant extent, at the NO_2 group which is unexpected on the basis of the magnitude of orbital overlap.[2a]

The electrophilic character of $\cdot OH$ radical is well documented;[2a,23-25] Eberhardt and Yoshida[2a] have shown that the $\cdot OH$ radical has a very low lying SOMO (singly occupied molecular orbital) and it will, therefore, interact mainly with the HOMO (highest occupied molecular orbital) of the aromatic compounds. SCF–MO (CNDO-2 and INDO) calculations of nitrobenzene have shown that the HOMO coefficients in the aromatic ring are very small (≤ 0.024) in agreement with the well-known resistance of nitrobenzene toward electrophilic substitution. Because of this small orbital overlap at all ring positions there may be little selectivity in the initial addition reaction and in presence of an effective oxidizing agent one may then obtain a close to statistical isomer distribution.

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