Anal. Calcd for $C_5H_7BrF_4N_2$: C, 23.94; H, 2.79; Br, 31.87; F, 30.27; N, 11.15. Found: C, 23.76; H, 2.59; Br, 31.54; F, 30.40; N, 11.37.

Registry No.—Tetrafluorohydrazine, 10,036-47-2; **6**, 96-11-7; *cis* **7**, 16101-27-2; *trans* **7**, 16101-28-3.

Acknowledgment.—The assistance of Mrs. Carolyn Haney in obtaining the nmr spectra and the interpretation of the data is appreciated. The support and encouragement of Dr. R. S. Yost is gratefully acknowledged.

Radiation-Induced Hydroxylation of Nitrobenzene in Dilute Aqueous Solution[1]

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The isomeric nitrophenols have been quantitatively determined by gas–liquid partition chromatography in irradiated solutions of dilute aqueous nitrobenzene. The relative rates of hydroxylation for $C_6H_5NO_2$ and $C_6D_5NO_2$ have been found to be identical and therefore the initial step of hydroxylation is the addition of $\cdot$OH to the aromatic ring The G values obtained for nitrophenols suggest preferential dimer formation. If the solvated electrons are not completely scavenged additional nitrophenols are produced by a complicated set of reactions involving the nitro-substituted hydroxycyclohexadienyl radical, the dimers, and their subsequent products. The mechanisms for these processes are discussed.

Aromatic compounds are easily and often selectively hydroxylated in nature by enzymes[2] whereas hydroxylation by chemical reagents is difficult and the mechanisms are complex.[3] Radiation-induced hydroxylation offers a somewhat simpler system since, in this case, the generation of hydroxyl radicals *in situ* avoids the necessity of adding an additional reagent to the system. The hydroxyl radical together with the solvated electron, hydrogen atom, hydrogen molecule, and hydrogen peroxide are the chemical species primarily formed by γ irradiation of water.[4,5] We have undertaken a systematic investigation of the radiation induced hydroxylation of monosubstituted aromatic compounds in dilute aqueous solutions. Our primary concern was to obtain meaningful data for isomeric distributions and partial rate factors, and to compare chemical and radiation-induced hydroxylations. We examined initially the effect of irradiation by γ rays on nitrobenzene in dilute aqueous solutions. In the course of our work it became apparent that the radiation chemistry of this system is somewhat more complicated than we anticipated. For this reason we are reporting the hydroxylation of nitrobenzene separately.

Experimental Section

Two separate cobalt-60 γ-irradiation facilities were used. The absorbed dose rates were determined to be 20.8×10^2 and 3.45×10^2 rads min^{-1} by the Fricke dosimeter taking $G(\text{Fe}^{3+}) = 15.5$.[6]

For the irradiation of air-saturated solution redistilled reagent grade nitrobenzene was dissolved in triply distilled water by vigorous shaking and its concentration was determined spectrophotometrically at 269 mμ.[7] The pH of the triply distilled water was adjusted by the addition of small volumes of concentrated sulfuric acid or sodium hydroxide to the required value. Argon, oxygen, and nitrous oxide saturated solutions were prepared by bubbling the high purity gas through the triply distilled water in the irradiation cell. The gas was introduced into the irradiation cell by the use of a hypodermic needle which was punched through a silicone septum and pushed close to the bottom of the cell. An outlet for the saturating gas was provided by inserting another needle through a second septum above the water level. The duration of the saturation was about 15–20 min and it was enhanced by frequent shaking. After saturation the needles were withdrawn and the required amount of nitrobenzene was introduced with a Hamilton gas-tight syringe and dissolved by vigrous shaking.

Deuterated nitrobenzene, $C_6D_5NO_2$, was obtained from Mallinckrodt Nuclear Corp. and its deuterium content was established to be 98% by mass spectroscopy.[8]

The conversion of nitrobenzene into products was kept at less than 1% to avoid secondary reactions. After the completion of irradiation a small portion of the solution (usually 10 ml) was analyzed for nitrite, nitrate, and hydrogen peroxide and the remainder (150 ml) was treated for nitrophenols and phenol.

Nitrite was analyzed by the Griess–Ilosvay test[9] and the nitrate was determined by the brucine method.[9] Standard sodium nitrate solutions were used to construct calibration curves.

Hydrogen peroxide was analyzed spectrophotometrically by the iodide method;[10] calibration curves were constructed using dilutions of stock solutions of hydrogen peroxide whose concentrations were standardized by B. D. H. standard ceric sulfate solution.[11] The irradiated solution, without the added reagents, was used as a blank for the spectroscopic determinations.

After adjusting the pH of the aqueous irradiated nitrobenzene solutions to 12.5 with sodium hydroxide, the solution was extracted with ether to remove the unreacted nitrobenzene. The pH of the aqueous layer was readjusted to 2.0 with HCl and was extracted twice with 100-ml portions of redistilled ether. These ether layers were concentrated by rotary evaporation to 5.0 ml at temperatures not exceeding 20° and were analyzed by gas–liquid partition chromatography. Using a 1-m glass column [0.25 i.d. packed with 2% Versamid 900 (F & M) on Chromasorb W] with temperature programming at 2.5°/min from 25° and at a flow rate of 115 cc of He/min,[12] the following retention times (in minutes) were obtained: *o*-nitrophenol, 30; phenol, 42; *m*-nitrophenol, 57; and *p*-nitrophenol, 62. Using the same column [but packed with a mixture of 2% Versamid on Chromosorb W (75%) and 1% 1,2,3,4-tetrakis(2-cyanoethoxy)butane on C-22 (25%)], the same temperature programming, and an identical He flow rate, the following retention times (in minutes)

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[1] Supported in part by the U. S. Atomic Energy Commission.

[2] R. O. C. Norman and J. R. L. Smith, "Oxidases and Related Systems," T. E. King, H. S. Mason, and M. Morrison, Ed., John Wiley and Sons, Inc., New York, N. Y., 1965, p 131.

[3] (a) J. R. L. Smith and R. O. C. Norman, *J. Chem. Soc.*, 2897 (1963); (b) R. O. C. Norman and G. K. Radda, *Proc. Chem. Soc.* (London), 138 (1962); (c) G. A. Hamilton, J. W. Hanifin, Jr., and J. P. Friedman, *J. Amer. Chem. Soc.*, **66**, 5266, 5269 (1966).

[4] The yields of these species at pH 7 are[5] $G_{\text{OH}} = 2.4$; $G_{e_{aq}^-} = 2.8 \pm 0.2$; $G_{\text{H}} = 0.6$; $G_{\text{H}_2} = 0.5$; $G_{\text{H}_2\text{O}_2} = 0.7$.

[5] E. J. Hart, *Ann. Rev. Nucl. Sci.*, **15**, 125 (1965), and references therein.

[6] J. W. T. Spinks and R. J. Woods, "An Introduction to Radiation Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 106.

[7] J. C. P. Schwarz, "Physical Methods in Organic Chemistry," Holden-Day Inc., San Francisco, Calif., 1964, p 147.

[8] We are indebted to Mr. G. Buzzard for this determination.

[9] D. F. Boltz, Ed., "Colorimetric Determination of Non-metals," Interscience Publishers, Inc., New York, N. Y., 1958.

[10] C. J. Hochanadel, *J. Phys. Chem.*, **56**, 587 (1952).

[11] E. C. Hurdis and H. Romeyer, Jr., *Anal. Chem.*, **26**, 320 (1954).

[12] T. S. Ma and Donald Spiegel, *Microchem. J.*, **10**, 61 (1966).

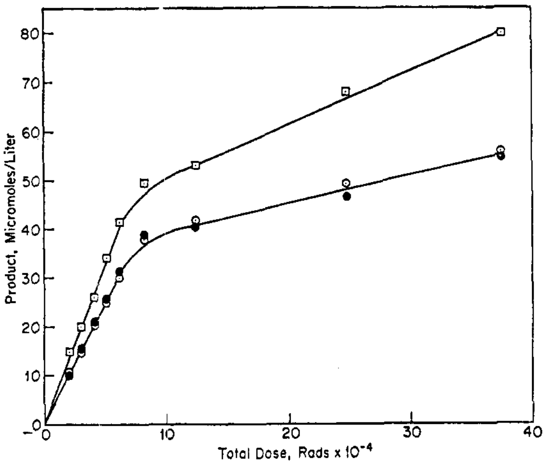

Figure 1.—Isomeric nitrophenol yields as a function of dose in the radiolysis of air-saturated aqueous 7 × 10^{-3} M nitrobenzene at pH 6.5: ⊙, *o*-nitrophenol; ●, *m*-nitrophenol; ⊡, *p*-nitrophenol.

were obtained: *o*-nitrophenol, 28, and phenol, 43. A thermal conductivity detector was used at a cell current of 160 mA or 195 mA. Known concentrations of the nitrophenols and phenol were used to obtain excellent linear calibrations. Furthermore, using synthetic mixtures of these nitrophenols and repeating the extraction and concentration techniques used for the analysis of the irradiated samples, the recovery of the compounds was 95–100%.

Results

The major products measured are the three isomeric nitrophenols, and their concentrations in an air-saturated solution at pH 6.5 as a function of total dose are plotted in Figure 1. The concentration of nitrophenols increases linearly with the dose up to 6.0 × 10^4 rads, at which point all the available oxygen has been used by its reaction with hydrogen atoms and hydrated electrons. From the initial slopes of the straight lines the G values have been calculated. At doses of 6–10 × 10^5 rads the irradiated solution became very dark, presumably owing to increased dimer formation. The nitrophenol yields were decreased by a factor of ten, and phenol was detected. For this reason all the reported G values were obtained from dose–yield plots for doses not exceeding 5 × 10^4 rads. The very sensitive Griess–Ilosvay test[9] gave negative results for nitrite ion. Nitrate ion yields were however quantitatively determined in the irradiated solutions.

Table I gives the yields of irradiated products at different pH values in aqueous air saturated solutions of 7 × 10^{-3} M nitrobenzene. The yields of nitrophenols are considerably higher than those previously reported in the X-ray irradiation of aqueous nitrobenzene, presumably owing to improvements in the method of analysis.[13]

The yields of products under different conditions are given in Tables II and III.

When 0.5 M methanol was added to the water, no nitrophenols were detected in the air-saturated solutions of 7 × 10^{-3} and 5 × 10^{-4} M nitrobenzene.

No detectable changes were observed in the product yields if irradiations were carried out at the two different dose rates (see Experimental Section).

Table I

Initial Yield of Irradiation Products at Different pH Values in Air-Saturated,[a] 7 × 10^{-3} M Aqueous Nitrobenzene

pH	*G* value[b] *o*-Nitrophenol	*m*-Nitrophenol	*p*-Nitrophenol	Nitrate ion
2.0	0.50	0.52	0.58	0.5
6.5	0.48	0.48	0.64	0.5
9.0	0.50	0.50	0.65	0.5
10.5	0.52	0.52	0.65	0.4
12.0	0.43	0.43	0.48	0.4

[a] [O_2] = 2.3 × 10^{-4} M. [b] The estimated error for the nitrophenol yields are ±5%, for nitrate ion it is ±15%.

Table II

Initial Yield of Nitrophenols at pH 6.5 in 7.3 × 10^{-3} M Aqueous Nitrobenzene

	G value[a] *o*-Nitrophenol	*m*-Nitrophenol	*p*-Nitrophenol
Air saturated[b]	0.48	0.48	0.64
Oxygen saturated[c]	0.52	0.44	0.38
Argon saturated	0.13	0.13	0.48
Nitrous oxide saturated[d]	0.37	0.15	0.67

[a] Estimated error for the nitrophenol yields are ±5%. [b] [O_2] = 2.3 × 10^{-4} M. [c] [O_2] = 1.0 × 10^{-3} M. [d] [N_2O] = 2.0 × 10^{-2} M.

Table III

Initial Yield of Irradiation Products at pH 6.5 in 5.0 × 10^{-4} M Aqueous Nitrobenzene

	G value[a] *o*-Nitrophenol	*m*-Nitrophenol	*p*-Nitrophenol	Hydrogen peroxide
Air saturated[b]	0.47	0.29	0.18	1.9
Oxygen saturated[c]	0.34	0.23	0.18	
Nitrous oxide[d] saturated	0.26	0.14	0.25	
Nitrous oxide[e] and oxygen	0.86	0.53	0.30	1.9

[a] Estimated error for the nitrophenol yields are ±5%; for phenol, ±15%; and for hydrogen peroxide, ±15%. [b] [O_2] = 2.3 × 10^{-4} M. [c] [O_2] = 1.0 × 10^{-3} M. [d] [N_2O] = 2.0 × 10^{-2} M. [e] [N_2O] = 1.45 × 10^{-2} M and [O_2] = 2.3 × 10^{-4} M.

p-Nitroso-N,N-dimethylaniline reacts exclusively with hydroxyl radical, and because of its high extinction coefficient it can conveniently be used as a competitor[14] for obtaining relative rates of hydroxyl radical attack. A plot of 1/G(*p*-nitroso-N,N-dimethylaniline) against [competitor]/[*p*-nitrosodimethylaniline] gave excellent straight lines. From the slopes of these lines the relative rates of hydroxylation of ethanol, nitrobenzene, and nitrobenzene-d_5 were determined.

By using the value of $k_{(OH\,+\,C_2H_5OH)}$ = 1.1 × 10^9 M^{-1},[15] $k_{(OH\,+\,C_6H_5NO_2)}$ was calculated to be (1.7 ± 0.2) × 10^9 M^{-1} sec^{-1}. The corresponding rate constant for the completely deuterated nitrobenzene, $k_{(OH\,+\,C_6D_5NO_2)}$, was found to be (1.8 ± 0.2) × 10^9 M^{-1} sec^{-1}.[16,17]

Discussion

The hydroxyl radical has a high electron affinity and, consequently, some electrophilic character in its

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(13) H. Loebl, G. Stein, and J. Weiss, *J. Chem. Soc.*, 2704 (1950).

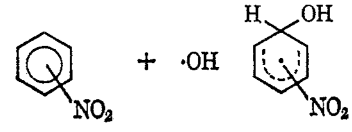
(14) I. Kraljic and C. N. Trumbore, *J. Amer. Chem. Soc.*, **76**, 2547 (1965).

(15) G. E. Adams, J. W. Boag, J. Currant, and B. D. Michael in "Pulse Radiolysis," J. H. Baxendale, M. Ebert, J. P. Keene, and A. J. Swallow, Ed., Academic Press Inc., New York, N. Y., 1965, p 131.

(16) The rate constant $k_{(OH\,+\,C_6H_5NO_2)}$ has been recently determined by pulse radiolysis to be 4.7 × 10^9 M^{-1} sec^{-1}.[17] This discrepancy, of course, does not invalidate the agreement between the rate constants for the OH attack on $C_6H_5NO_2$ and $C_6D_5NO_2$.

(17) K.-D. Asmus, B. Cercek, M. Ebert, A. Henglein, and A. Wigger, *Trans. Faraday Soc.*, **63**, 2435 (1967).

reaction with aromatic compounds.[2,18] It can either add to an aromatic nucleus to form a cyclohexadienyl-type radical or abstract a hydrogen atom from it. The presence of phenol,[13] biphenyl,[13] and nitrate ion in the irradiation products might indicate the formation of a phenyl radical. Indeed, this has been suggested in connection with the hydroxylation mechanism of nitrobenzene.[13,19] Recent work, however, on the oxidation of benzene by Fenton's reagent[3a] and on the pulse radiolysis of dilute aqueous benzene solutions[20] has conclusively shown that in the case of benzene the formation of hydroxycyclohexadienyl radical is the initial step in hydroxylation. The equivalence of the hydroxylation rate constants for nitrobenzene and nitrobenzene-d_5 (see results) is compatible only with the initial formation of a nitro-substituted hydroxycyclohexadienyl radical (see eq 1).



I

(1)

Radical I has been recently observed in the pulse radiolysis of dilute aqueous nitrobenzene and the rate constant for eq 1 was calculated to be $4.7 \times 10^9\ M^{-1}\ \text{sec}^{-1}$.[17]

The formation of cyclohexadienyl-type intermediates both in electrophilic[21a] and nucleophilic[21b] aromatic substitutions has been described as initial steps for these reactions. It seems, therefore, that both ionic and radical substitutions of an aromatic carbon atom involve rehybridization of the carbon atom at the point of attack.

The hydrated electron also reacts with nitrobenzene according to eq 2 with a rate constant of 3×10^{10}

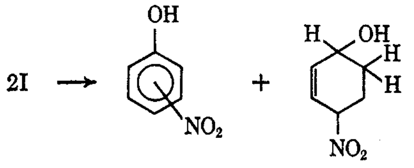
$$C_6H_5NO_2 + e_{aq}^- \longrightarrow C_6H_5NO_2^- \qquad (2)$$

$M^{-1}\ \text{sec}^{-1}$.[22] In an air-saturated solution at the higher nitrobenzene concentration ($7 \times 10^{-3}\ M$) both eq 1 and 2 competitively prevail. At the lower concentration of nitrobenzene ($5 \times 10^{-4}\ M$) in the presence of N_2O more than 90% of eq 2 is suppressed. This latter situation is somewhat simpler and therefore it will be discused first.

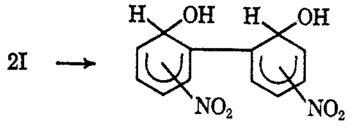
In an N_2O-saturated solution the hydrated electron is scavenged;[23] the rate constant for eq 3 is 9×10^9

$$e_{aq}^- + N_2O \longrightarrow \cdot OH + N_2 + OH^- \qquad (3)$$

$M^{-1}\ \text{sec}^{-1}$, thus at $5 \times 10^{-4}\ M$ nitrobenzene concentration only some 8% of the nitrobenzene is expected to react according to eq 2. Furthermore, since every e_{aq}^- is converted into a hydroxyl radical, the yields of hydroxylated products are to be expected to approach the value of $G_{OH} + G_{e_{aq}^-}$. The radiation-induced hydroxylation of benzene in nitrous oxide saturated aqueous solution has born out this expectation.[24] The total yields of nitrophenols in the nitrous oxide-saturated system is 0.65 (Table III), a G value considerably smaller than expected. This must mean that I and possibly other substituted hydroxycyclohexadienyl radicals decompose in a different manner than the unsubstituted hydroxycyclohexadienyl radical. In a recent work eq 1 was suggested to be followed by eq 4 and 5.[17] The absorbance of the final products, the



(4)



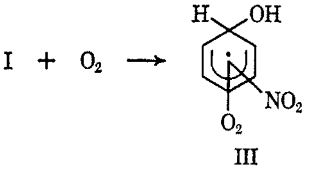
II

(5)

isomeric nitrophenols, was found to be only one-third of that due to I at 4100 Å.[17] Furthermore since 2 mol of I only give 1 mol of nitrophenol (eq 4) the G value for nitrophenols was estimated to be not greater than 0.75.[17] The present results are clearly in good agreement with this postulation (Table III). The yield of *m*-nitrophenol in this system is very much smaller than that of either the *ortho* or *para* isomer in accord with the expectation from the absorption spectra of pulsed irradiated aqueous nitrobenzene at different pH values.[17]

When oxygen is present in addition to nitrous oxide as a scavenger, eq 6[25] and 7 must also be considered.

$$e_{aq}^- + O_2 \longrightarrow O_2^- \qquad (6)$$



III

(7)

Equation 6 scavenges the solvated electron in addition to eq 3. Equation 7 has been demonstrated and its observed rate constant is $(2.5 \pm 0.3) \times 10^6\ M^{-1}\ \text{sec}^{-1}$.[17] It is not unreasonable to expect that the formation of dimers (II) from III is less favorable than from I. The yield of nitrophenols in the nitrous oxide-oxygen saturated system is almost twice as high as in the absence of oxygen (Table III) which supports this theory. The decrease in the percentage of *p*-nitrophenol produced in the N_2O–O_2 system in relation to the N_2O system tends to suggest that in III the oxygen is preferentially situated in the *para* position.

In a recent pulse radiolysis study it was demonstrated that the initially formed dihydroxycyclohexadienyl radical subsequently yielded phenoxyl radical either by OH^- or H^+ removal.[26] The presence of nitrate ions in the irradiated samples of aqueous nitrobenzene tend to suggest that a similar mechanism might operate to remove HNO_2 from I to form the phenoxyl

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[18] M. Anbar, D. Meyerstein, and P. Neta, *J. Phys. Chem.*, **70**, 2660 (1966).

[19] H. Loebl, G. Stein, and J. Weiss, *J. Chem. Soc.*, 2074 (1949).

[20] L. M. Dorfman, I. A. Taub, and R. E. Bühler, *J. Chem. Phys.*, **36**, 3051 (1962).

[21] (a) E. Berliner, *Progr. Phys. Org. Chem.*, **2**, 253 (1964); (b) *ibid.*, **1**, 31 (1963).

[22] K.-D. Asmus, A. Wigger, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, **70**, 862 (1966).

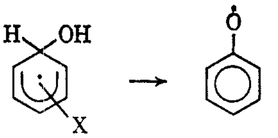
[23] G. Scholes and M. Simic, *J. Phys. Chem.*, **68**, 1731 (1964); F. S. Dainton and D. B. Peterson, *Proc. Roy. Soc.*, **A267**, 443 (1962).

[24] Unpublished results of J. H. Fendler and G. L. Gasowski.

[25] S. Gordon, E. J. Hart, M. Matheson, J. Rabani, and J. K. Thomas, *J. Amer. Chem. Soc.*, **85**, 1374 (1963); E. J. Hart, J. K. Thomas, and S. Gordon, *Radiat. Res. Suppl.*, **4**, 74 (1964).

[26] E. J. Land and M. Ebert, *Trans. Faraday Soc.*, **63**, 1181 (1967).

radical. The HNO_2 radical then rapidly oxidizes to the nitrate ion. The observation of chloride ion in the irradiated aqueous solution of chlorobenzene[27] and phenol in irradiated aqueous anisole[24] support a general mechanism in which the formation of phenoxyl radical is a subsequent step in the rearrangement of of any substituted hydroxycylohexadienyl radical.



In an air or oxygen saturated solution of aqueous 7×10^{-3} M nitrobenzene and in the N_2O-saturated solution at the same nitrobenzene concentration not more than 10% and approximately 50%, respectively, of the hydrated electrons are scavenged (eq 6 and 3). Contrary to expectations the yield of nitrophenols under these conditions is considerably higher (Table I) than in the system where only 10% of the hydrated electron was allowed to react with the nitrobenzene. This is only explicable in terms of the formation of additional nitrophenols *via* eq 2. Since in the presence of 0.5 M methanol, which effectively scavenges all the hydroxyl radicals, no nitrophenol was formed (see results), one must conclude that a complicated set of reactions exist between I and II and/or between their respective rearranged products which ultimately results in the preferential formation of nitrophenols instead of dimers.

Changes in the pH have only small effects on the yields although at pH 12 nitrophenols have smaller G values than at other pH values (Table I). This is reasonable since at higher hydroxide ion concentrations the reaction in eq 8 becomes more important and the O^- formed is not so reactive as the OH^- radical.[28]

$$OH^- + OH \longrightarrow H_2O + O^- \qquad (8)$$

We had hoped to detect the presence of aromatic peroxides and hydroperoxides by observing the difference in hydrogen peroxide yields obtained by the iodide and titanium sulfate methods since only the latter test is specific for inorganic peroxides.[20] At the low doses employed hydrogen peroxide was not formed in sufficient concentration to be detectable by the titanium sulfate method. The obtained G values (Table III) are nevertheless in accordance with the hydrogen peroxide yields determined in an irradiated solution of aqueous benzene.[20]

The formation of dimers and generally the presence of numerous side reactions appear to be a general case in the radiation-induced hydroxylation of monosubstituted aromatic compounds in dilute aqueous solutions.[24] Of the disubstituted compounds studied so far the irradiation of p-nitrophenol seems to present a clearer picture. The G value for 2-hydroxy-4-nitrophenol is 2.95.[29] It is possible that the formation of dimers in this system is not favorable.

The isomeric percentage distributions of nitrophenols and partial rate factors obtained in this study are compared to other chemical hydroxylations[2] in Table IV. The *ortho* and *para* positions for the radiation induced hydroxylations of dilute aqueous nitrobenzene are activated to a greater extent than the *meta* position. The selective activation of these two positions is explicable in terms of the enhanced conjugation of the directing nitro group with the benzene ring; a similar situation exists in the homolytic phenylation of nitrobenzene.[30] Whereas the qualitative agreement in the partial rate factors of chemical and radiation-induced hydroxylations is reasonable, owing to the uncertainties of the intricate mechanism of both systems, quantitative correlations are not warranted at present.

TABLE IV

ISOMER DISTRIBUTION OF NITROPHENOLS AND PARTIAL RATE FACTORS FOR THE HYDROXYLATION OF NITROBENZENE

	Isomer distribution, %			—Partial rate factors[a]—		
	o	*m*	*p*	o_f^R	m_f^R	p_f^R
Radiaton induced[b]	51	31	18	1.80	1.10	1.91
Radiation induced[c]	40	21	39	1.42	0.71	2.76
Radiation induced[d]	50	31	19	1.77	1.10	1.34
Radiation induced[e]	30	30	60	1.06	1.06	4.25
Fenton reagent[f]	24	30	46	0.85	1.06	3.26
Hamilton reagent[f]	30	41	29	1.06	1.45	2.05

[a] $o_f^R = k_{(C_6H_5NO_2 + \cdot OH)}/{}^1/_6k_{(C_6H_6 + \cdot OH)} \times$ % o-nitrophenol/2 × 100; $m_f^R = k_{4(C_6H_5NO_2 + \cdot OH)}/{}^1/_6k_{4(C_6H_6 + \cdot OH)} \times$ % m-nitrophenol/2 × 100; $p_f^R = k_{(C_6H_5NO_2 + \cdot OH)}/{}^1/_{6(C_6H_6 + \cdot OH)} \times$ % p-nitrophenol/100. [b] $[C_6H_5NO_2] = 5 \times 10^{-4}$ M, $[N_2O] = 1.45 \times 10^{-2}$ M, $[O_2] = 2.3 \times 10^{-4}$ M. [c] $[C_6H_5NO_2] = 5 \times 10^{-4}$ M, $[N_2O] = 2.0 \times 10^{-2}$ M. [d] $[C_6H_5NO_2] = 5 \times 10^{-4}$ M, air saturated. [e] $[C_6H_5NO_2] = 7 \times 10^{-3}$ M, air saturated. [f] See ref 3a.

Registry No.—Nitrobenzene, 98-95-3; o-nitrophenol, 88-75-5; m-nitrophenol, 554-84-7; p-nitrophenol, 100-02-7.

Acknowledgments.—It is a pleasure to acknowledge very helpful discussions with Drs. K.-D. Asmus, E. J. Fendler, R. H. Schuler, D. Schulte-Frohlinde, I. A. Taub, and J. M. Warman, and the competent assistance of Mr. G. W. Klein.

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