Products of the Radiolysis of Water Containing Benzene and Nitric Acid

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Radiolysis of water saturated with benzene and containing dissolved air has been studied by many workers$^{1-6)}$. Stein and Weiss$^{1)}$ reported that phenol and hydrogen peroxide are formed until oxygen is depleted, then, the formation of phenol begins to slow down, while diphenyl starts to appear in increasing yield. The effect of pH on the phenol yield

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1) G. Stein and J. Weiss, *J. Chem. Soc.*, **1949**, 3245.

2) T. J. Sworski, *J. Chem. Phys.*, **20**, 1817 (1952).

3) T. J. Sworski, *Radiation Research*, **1**, 231 (1954).

4) J. H. Baxendale and D. Smithies, *J. Chem. Soc.*, **1959**, 779.

5) P. V. Phung and M. Burton, *Radiation Research*, **7**, 199 (1957).

6) E. Collinson and A. J. Swallow, *Chem. Revs.*, **56**, 505 (1956).

is only slight, as might be expected if the mechanism were a free radical one[1,4]. On the other hand, the yield of diphenyl is significantly lower at high pH[4], and this result is difficult to understand. All their experiments were carried out either in aqueous sulfuric acid or in phosphoric acid. No specific influence was observed at the same pH with the two different anions in their experiments. Meanwhile, we found in the irradiation of benzene in nitric acid solution that nitrophenol formed and diphenyl did not appear. The present paper provides data on the radiation induced reaction of water containing benzene and nitric acid at various concentrations.

Experimental

Irradiations.—The γ-radiation was provided by either a 1000 or a 3800 curie cobalt-60 source. The rate of energy absorption in solution was determined with the Fricke ferrous sulfate dosimeter taking G as 15.6[7]. All the irradiations were carried out at ambient temperature between 15 to 25°C.

Preparation of Solutions.—Benzene was purified by an ordinary method. Distilled water and reagent grade nitric acid were used. Actually water shaken with benzene at room temperature is found to dissolve 0.022 mol. per liter. Stock solution of irradiated sample was prepared by mixing standard benzene solution and nitric acid solution to the final desired concentration for both benzene and nitric acid. Solutions used for irradiation were made containing dissolved air.

Determination of *p*-Nitrophenol.—The determination of *p*-nitrophenol was carried out by colorimetry. After adjusting the pH of the irradiation solution, which, if necessary, was filtered off, the absorbance of *p*-nitrophenolate ion was measured spectrophotometrically at 400 mμ, and also determined by pentacyanoammineferroate.

Determination of *o*-Nitrophenol.—The formation of cobalt-chelate compound was used to the determination of *o*-nitrophenol. The *o*-nitrophenol was nitrosated by reduction with calcium chloride and zinc powder and the isolated nitroso compound was treated with a cobalt salt in an acetate buffer solution.

Results and Discussion

Nitric acid solutions of benzene were irradiated with Co-60 gamma rays by a varying dose rate from 2.9×10^3 to 5.6×10^4 r/hr. The yield of *p*-nitrophenol produced is shown in Table I. As is shown in Table I, the yield of *p*-nitrophenol decreases with increasing dose rate. The observed decrease of yield with dose rate may be ascribed to the increased probability of the recombination between generated radicals at the higher dose rate, although its exact nature is not yet clear.

TABLE I. THE YIELD OF *p*-NITROPHENOL FROM THE IRRADIATED SOLUTIONS

Dose rate r/hr. $\times10^{-3}$	G-Value
56	0.47
28.2	0.57
16.4	0.71
11.5	0.79
8.1	0.84
5.9	0.86
5.2	0.85
3.8	0.92
2.9	0.96

0.8N HNO_3 saturated benzene solution, 0.022 mol./l. Irradiation time, 18 hr.

Nitric acid concentration dependence for the yield of *p*-nitrophenol at the fixed dose of 3×10^6 r is shown in Table II. The yield of *p*-nitrophenol decreases with increasing nitric acid concentration.

The quantitative results indicate the preferential formation of *p*-nitrophenol to that of *o*-nitrophenol. The formation of *p*-nitrophenol is proportional to the energy absorbed, and the yield depends on dose rate and nitric acid concentration.

TABLE II. DEPENDENCE OF NITRIC ACID CONCENTRATION

Nitric acid concentration	Formation of *p*-nitrophenol	
N	mol./l. $\times10^4$	G-Value
1.7	7.95	0.28
0.86	10.7	0.37
0.43	15.9	0.55
0.23	18.2	0.63

Irradiation time, 6 hr. Dose rate, 5×10^5 r/hr. Benzene concentration, 0.016 mol./l.

The action of ionizing radiations on dilute aqueous solutions results in formation of free radicals according to

$$H_2O \rightsquigarrow H+OH \qquad (1)$$

On the other hand, the gamma radiolysis of nitric acid solutions indicates that nitric acid is decomposed by radical mechanism as given by the following equation[8].

$$HNO_3 \rightsquigarrow HNO^*_3 \rightarrow OH+NO_2 \qquad (2)$$

The radical process is, as direct action effects are generally considered to be, directly proportional to the concentration. The qualitative results are best explained by assuming that the primary reaction 1 and reaction 2, resulting in the formation of hydroxyl radical, which attacks on a benzene molecule.

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[7] C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, 21, 880 (1953).

[8] H. A. Mahlman, *J. Chem. Phys.*, 35, 936 (1961).

$$C_6H_6 + OH \rightarrow C_6H_5 + H_2O \qquad (3)$$

The phenyl radical formed can reacts with hydroxyl radical, yielding phenol

$$C_6H_5 + OH \rightarrow C_6H_5OH \qquad (4)$$

or with NO_2 radical, giving nitrobenzene.

$$C_6H_5 + NO_2 \rightarrow C_6H_5NO_2 \qquad (5)$$

In fact, it was found by gas chromatography that the ether extraction from the irradiated solutions contained nitrobenzene. But no phenol was observed in the irradiated solutions. Consequently, the phenol furthermore reacts with hydroxyl radical to forms phenol radical,

$$C_6H_5OH + OH \rightarrow C_6H_4OH + H_2O \qquad (6)$$

which is readily scavenged by NO_2 radical.

$$C_6H_4OH + NO_2 \rightarrow C_6H_4(OH)NO_2 \qquad (7)$$

The phenol is effectively converted to *p*-nitrophenol. While, irradiation of nitrobenzene in nitric acid solution did not give *p*-nitrophenol.

The decrease of *G*-value at higher acid concentration is probably due to the formation of nitrobenzene, which is increases with increasing NO_2 radicals from nitric acid irradiation. This becomes important at higher concentration of nitric acid, and leads to the formation of *p*-nitrophenol in a lower yield.

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