The Thermal and Radiation Oxidation of Benzene to Phenol in Aqueous Solutions Containing Metal Ions at Elevated Temperatures. VI. The By-products of Benzene Oxidation

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The oxidation of benzene catalyzed by metal ions has been discussed in previous papers,[1-3] in which the phenol yield has been shown to increase very little with the rise in temperature above 170°C. The present paper will analyze the by-products and compare them with those of phenol oxidation, which were reported on in Part V.[4]

Unpurified benzene was oxidized thermally in aqueous solutions of 0.01 M ferrous and cupric sulfates, while purified benzene was oxidized with gamma-ray irradiation in these solutions, both procedures being the same as in previous papers.[1,3] The products were then analyzed by means of gas chromatography as in Part V.[4] The amounts produced are shown in Fig. 1 for the ferrous solution and in Fig. 2 for the cupric solution, with open marks representing unpurified benzene and solid marks, purified benzene respectively. In the figures, the amounts of phenol dissolved in the aqueous phase, as analyzed by gas chromatography, are shown by triangles (◬ and ▲). They are somewhat smaller than the amounts analyzed by optical absorption after ether extraction as in Parts II[1] and IV[3] and shown by circles (⊙ and ●). The amounts of acetic acid produced, shown by squares (⊡ and ■), increased with the rise in temperature, even at 220°C, at which point the amount of phenol did not increase so much. The amounts of acetaldehyde produced, shown by crosses (×) for unpurified benzene and by circle-crosses (⊗) for purified benzene, did not increase at temperatures higher than 200°C, as in the case of phenol. The other products which had been found in the decomposition of phenol in Part V[4] were also detected in the present study. Formaldehyde and acetone were found to be in the greatest quantity by about 1.5×10^{-6} mole at 200°C.

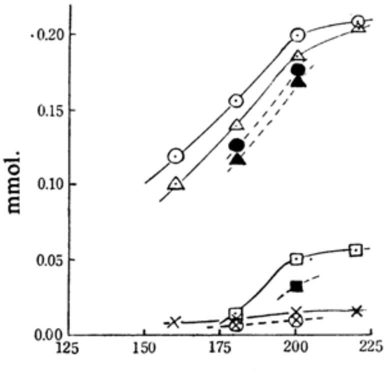

Fig. 1. Amounts of products produced in the aqueous solution of ferrous sulfate for the thermal oxidation of unpurified benzene (open marks and ×) and the radiation oxidation of purified benzene (solid marks and ⊗) : phenol by optical absorption, ⊙ and ●; phenol by gas chromatography, ◬ and ▲; acetic acid by GC, ⊡ and ■; and acetaldehyde by GC, × and ⊗.

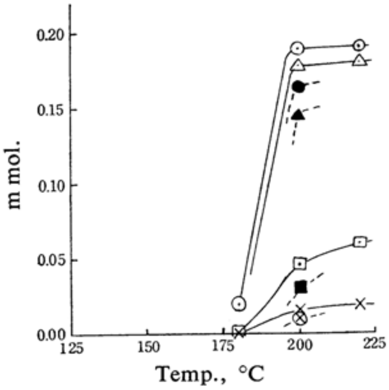

Fig. 2. Amounts of products produced in the aqueous solution of cupric sulfate; marks are the same as in Fig. 1.

When these results are compared with those in Part V, it may be concluded that the phenol produced is violently decomposed to acetic acid through acetaldehyde at high temperatures. That is, the saturation of the phenol yield at elevated temperatures is neither due to the self-inhibition effect of phenols on the oxidation

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[1] H. Hotta, A. Terakawa, K. Shimada and N. Suzuki, This Bulletin, 36, 721 (1963).

[2] H. Hotta, N. Suzuki and A. Terakawa, ibid., 36, 1255 (1963).

[3] N. Suzuki and H. Hotta, ibid., 37, 224 (1964).

[4] K. Shimada, N. Suzuki, N. Itatani and H. Hotta, ibid.. 37, 1143 (1964).

reactions,[5,6] nor to some termination and competing reactions with the chain-carrying radicals.[1] No biphenyl was detected for any of the ether extracts from the aqueous and benzene phases or in the inorganic precipitates after the reaction; gas chromatography with a PEG column at 180°C was the method employed.

Dihydroxybenzene, which was detected by thin-layer chromatography in Part V,[4] was found, by optical absorption for the thermal oxidation of benzene, in the ferrous sulfate solution by Terakawa et al.[7]

The presence of aldehydes among the oxidation products suggests that the reduction of ferric ions to ferrous ions, as seen in Part II,[1] is partly due to their reactions with aldehydes, not only to those with hydroperoxides, as has been discussed previously.[3]

The temperature dependences of the phenol yield in Figs. 1 and 2 are somewhat different from those in previous papers.[1,3] The present yields are somewhat smaller than those in the previous ones at the corresponding temperature, and they increase even at the temperature where there was saturation previously.[1,3] This is due to the difference of impurities in benzene, as has been discussed in Part IV.[3] In fact, the present unpurified benzene is rather pure, as may be seen by comparing Table I (the result of gas chromatography using a TCP-column at 70°C) with Table I of Part IV.[3]

TABLE I. IMPURITIES IN UNPURIFIED BENZENE, M

Carbon disulfide	2.7×10^{-4}
n-Hexane	1.7×10^{-4}
Cyclohexane	trace
Cyclohexene	trace
Thiophene	$<6\times10^{-4}$
Toluene	1.8×10^{-3}
Xylene	0

As may be seen in Figs. 1 and 2, phenol is produced from the purified benzene, which gave no appreciable peak of impurities in gas chromatography, unlike as in Part IV.[3] Therefore, the idea that the oxidation is initiated by benzene itself, as was assumed in Part II,[1] cannot be discarded, even if the impurities promote the oxidation process.

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[5] K. U. Ingold, *Chem. Revs.*, 61, 563 (1961).

[6] M. A. Proskurnin and Y. M. Kolotyrkin, *Proc. 2nd U. N. Conf., Geneva*, 29, 52 (1961).

[7] A. Terakawa, Y. Hosaka, M. Nitto and T. Hirayama, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), 66, 1328 (1963).