The Thermal and Radiation Oxidation of Benzene to Phenol in Aqueous Solutions Containing Metal Ions at Elevated Temperatures. V.
The Thermal Oxidation of Phenol and Maleic Acid

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The thermal oxidation of phenol in aqueous solutions was studied under the same conditions as for that of benzene to phenol in order to understand the benzene oxidation reported on in previous papers,[1] for the phenol produced might be also oxidized successively to other compounds. The oxidation of maleic acid was also studied with reference to this subject.

Experimental

Oxidation Procedure. — 5.35×10^{-2} M of phenol was dissolved in neutral and 0.1 N sulfuric acid solutions, to which ferrous, ferric and cupric sulfates were then added by 0.01 M as metal ions. These solutions were oxidized for 30 min. at 100∼200°C under an oxygen pressure of 30 atmospheres (at room temperature) by means of that procedure mentioned in Part II.[2] For reference, the same experiment was also carried out without any metal ions. This initial concentration of phenol is about 2∼3 times as great as the largest amount of phenol produced in the previous oxidation of benzene.[2]

Analytical.—After a thermal oxidation, the aqueous solutions were quantitatively analyzed directly by gas chromatography using a polyethylene-glycol (PEG 6000) column at the several temperatures (cf. Table I), depending upon the products to be analyzed. The order of the substance described in Table I is that of their retention time. Some of their peaks were assigned by other methods (to be mentioned later) as well as by the retention time. Some products were also identified by thin-layer chromatography.

TABLE I. TEMPERATURE OF PEG COLUMN, °C

Carbon dioxide	70
Acetaldehyde	70
Acetone	70
Formaldehyde	100
Acetic acid	130
Formic acid	130
Phenol	180

The concentration of iron species in the solution after the reaction was determined by the same methods as in Part II.[2]

Results

The results in all the figures except Figs. 2, 3 and 9 are shown by circle (⊙ and ●), triangle (◬ and ▲) and square (▣ and ■) marks for ferrous, ferric and cupric sulfates respectively. The open marks and solid lines are for the neutral solutions, while the solid marks and dotted lines are for the 0.1 N sulfuric acid solutions. The results without any metal ion are shown by crosses (×) for the aqueous solution and by circle crosses (⊗) for the 0.1 N sulfuric acid solution.

Phenol and Metal Ions after Reaction.—The amounts of phenol after reaction are shown in Fig. 1. The results can be interpreted in the terms used for the effect of metal ions on the benzene oxidation in previous papers.[1,2] The decomposition of phenol is suppressed in the acidic solutions, in which the concentration of ions is lowered. The effect of cupric sulfate can be understood by the fact that the concentration is high even at elevated temperatures,

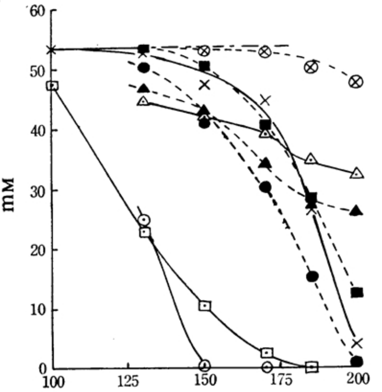

Fig. 1. Amounts of phenol after reaction in the solutions of ferrous (⊙ and ●,) ferric (◬ and ▲) and cupric (▣ and ■) sulfates, and without any metal ion (× and ⊗). The results of the aqueous solutions are represented by open marks and crosses (×), and those of the 0.1 N sulfuric acid solutions by solid marks and circle crosses (⊗).

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* From whom reprints should be requested.

1) N. Suzuki and H. Hotta, This Bulletin, 37, 244 (1964).

2) H. Hotta, A. Terakawa, K. Shimada and N. Suzuki, ibid., 36, 721 (1963).

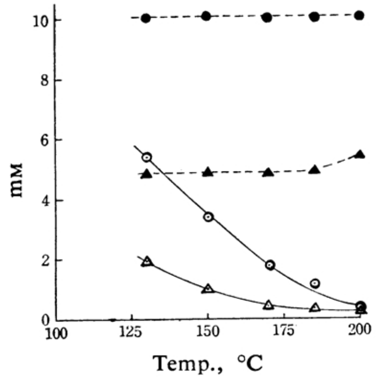

Fig. 2. Concentrations of iron species (⊙ and ●) and ferrous species (△ and ▲) after reaction in the ferrous sulfate solutions. Open marks are for the neutral solution, and solid marks for the 0.1 N sulfuric acid one.

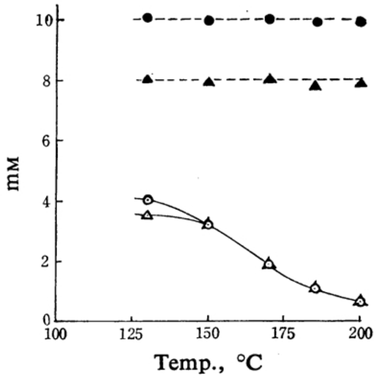

Fig. 3. Concentrations of iron and ferrous species after reaction in the ferric sulfate solutions. Marks are the same as in Fig. 2.

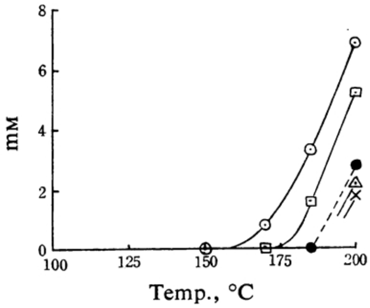

Fig. 4. Amounts of acetic acid produced in the various solutions. Marks are the same as in Fig. 1.

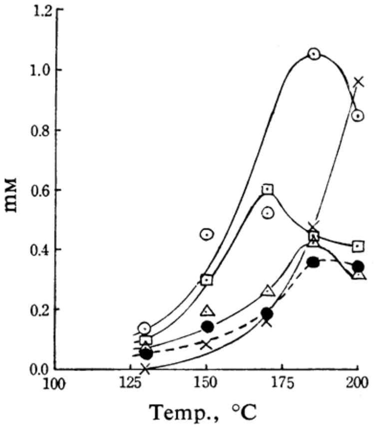

Fig. 5. Amounts of acetaldehyde produced in the various solutions. Marks are the same as in Fig. 1.

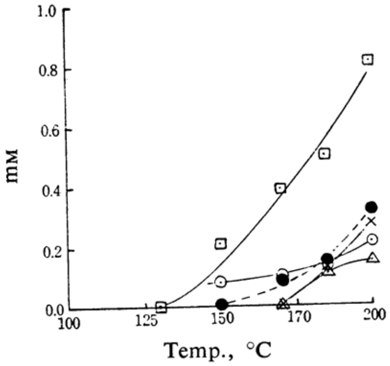

Fig. 6. Amounts of formaldehyde produced in the various solutions. Marks are the same as in Fig. 1.

unlike iron salts.[1]

The total concentrations of iron species (⊙ and ●) and the contents of ferrous species (△ and ▲) dissolved in the solutions of ferrous and ferric sulfates after reaction are shown in Figs. 2 and 3 respectively. The open marks are for the neutral solutions, while the solid marks for the 0.1 N sulfuric acid solutions.

Acetic and Formic Acids.—The amounts of acetic acid produced are shown in Fig. 4. Acetic acid was identified by the mass-spectrum of the fraction obtained by gas chromatography, the chemical shift of its unclear magnetic resonance spectrum, and the behavior for extraction procedure, as well as by the retention time of the gas chromatography. It was also confirmed by the presence of acetaldehyde among the products, as will be mentioned below.

There was a peak other than that of acetic acid for the gas chromatography of the samples oxidized at 200°C. This is supposed to be of formic acid judging from the retention time and the behavior of the extraction procedure, especially, the fact that the peak disappears when extracted by ether.

Aldehydes and Acetone. — The amounts of acetaldehyde and formaldehyde are shown in Figs. 5 and 6 respectively. The amounts of acetone produced are also shown in Fig. 7.

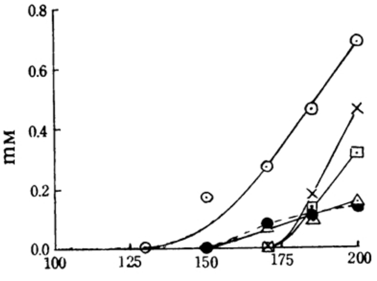

Fig. 7. Amounts of acetone produced in the various solutions. Marks are the same as in Fig. 1.

The carbonyl compounds were identified as their 2,4-dinitrophenyl hydrazone according to Johnson and Scholes.[3] They gave two absorption peaks at 360 and 560 mμ in the ethanolic alkaline solution dissolved after having been extracted into carbon tetrachloride. The former peak is usually given by monoaldehydes, and the latter by glyoxal and *p*-quinone. The uncorrected melting points of the hydrazones, given from the sample oxidized at 200°C in the aqueous solution of cupric sulfate, were 138∼141°C and 160°C for the fraction dissolved in methanol, and 270∼280°C for the insoluble fraction respectively. The melting points of the related hydrazones in the literature[4] are listed in Table II.

TABLE II. MELTING POINT OF 2,4-DINITROPHENYL HYDRAZONE DERIVATIVES, °C

Acetone	126
Acetaldehyde	147, 168
Formaldehyde	166
p-Quinone	267∼268
Glyoxal	328

The reduction of ferric ions to ferrous ions, as seen in Figs. 2 and 3, is due not only to their reactions with aldehydes, but also to those with hydroperoxides in the chain oxidation process, as has been pointed out in our previous papers;[1] that is,

$$\mathrm{ROOH} + \mathrm{M}^{2+} = \mathrm{ROO} + \mathrm{H}^{+} + \mathrm{M}^{+}$$

Carbon Dioxide.—The concentrations of carbon dioxide dissolved in the aqueous phase at the first day after reaction are shown in Fig. 8. They have been estimated approximately according to Seidell's textbook.[5]

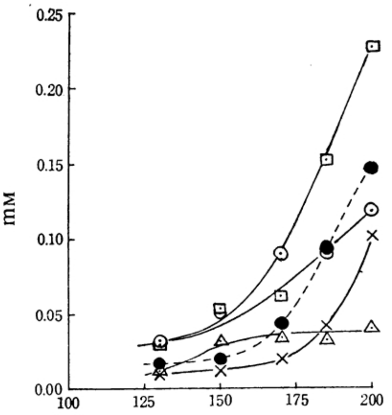

Fig. 8. Concentrations of carbon dioxide dissolved in the aqueous solutions at the first day after reaction. Marks are the same as in Fig. 1.

Thin-layer Chromatography.—Some products were detected by thin-layer chromatography using silica gel as an adsorbent on a glass plate[6] as follows (the detailed results will be described elsewhere).

When the sample, oxidized at 130°C in the aqueous solution of ferrous sulfate, was developed on the plate with a solvent composed of benzene 75+ethyl formate 24+formic acid 1, there were three spots of low R_f-values and two spots of high R_f-values. The former spots, colored by bromocresol green, were identified as oxalic, maleic and fumaric acids, and the latter spots, colored by a 5% iodine solution of ethanol, as *o*- and *p*-dihydroxybenzenes, from their R_f-values. The sample, oxidized at 200°C, gave only the spot of oxalic acid, suggesting that all the above products except oxalic acid decomposed at the higher temperature. *o*- and *p*-Dihydroxybenzenes have been reported to be found in the aqueous oxidation of phenol by Fenton's reagent or by X-rays at room temperature.[7]

Discussion

When the production of the decomposition products is compared with the consumption of phenol in Fig. 1, the amounts of the decomposition products are found to increase at higher temperatures, at which almost a part of phenol is consumed, suggesting that there are some fairly stable intermediates. This is shown clearly by the results concerning the aqueous solution of ferrous sulfate.

Since maleic and fumaric acids are detected by thin-layer chromatography, the oxidation

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[3] G. R. A. Johnson and G. Scholes, *Analyst*, **79**, 217 (1954).

[4] "Beilsteins Handbuch der Organische Chemie," XVI Zweittes Ergz., Springer-Verlag, Berlin (1951).

[5] A. Seidell, "Solubilities of Inorganic and Metal-organic Compounds," Vol. 1, D. Van Nostrand Co., New York (1953).

[6] E. Stahle, *Pharmazie*, **11**, 633 (1956); *Chemker Ztg.*, **82**, 323 (1958).

[7] G. Stein and J. Weiss, *J. Chem. Soc.*, **1951**, 3265.

of these acids (4.33×10^{-2} M) in the aqueous solution of ferrous sulfate by means of the same procedure as was used for phenol was examined by gas chromatography and by the absorptiometry of 2, 4-dinitrophenylhydrazone derivatives. The results, shown in Fig. 9, indicate that maleic acid gave acetic acid, acetaldehyde and formaldehyde. However, since fumaric acid is very stable, it did not give these products except for a trace amount of acetaldehyde. Therefore, it is likely that maleic acid is the stable precursor of these products in the oxidation of phenol. This is also supported by the fact that the amounts of acetic acid and aldehydes increase with the rise in temperature, while maleic and fumaric acids decrease at higher temperature, as is seen in thin-layer chromatography. Acetone was not given by these acids.

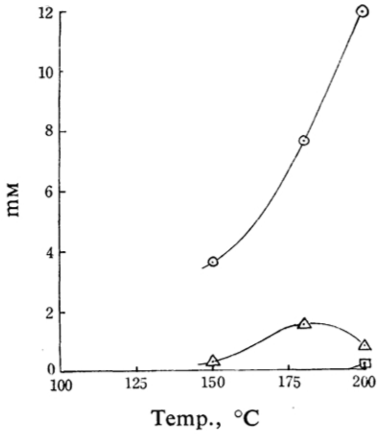

Fig. 9. Amounts of products from maleic acid (4.33×10^{-2} M) in the aqueous solution of ferrous sulfate; acetic acid (⊙), acetaldehyde (△) and formaldehyde (▣).

According to Bernatek et al.,[8-10] the ozonolysis of phenols, i. e., phenol, catechol, resorcinol and quinol, gives carbon dioxide, formic acid, oxalic acid and glyoxal, while that of *p*-benzoquinone gives formic acid, mesooxalic dialdehyde, glyoxylic acid, oxalic acid, maleic acid and carbon dioxide. However, they did not detect acetic acid and acetone.

Summary

The products of the oxidation of phenol in the aqueous solution (100~200°C) were analyzed by gas chromatography and by thin-layer chromatography. The amounts of the decomposition products, acetic acid, formic acid, acetaldehyde, formaldehyde, acetone and carbon dioxide, increase with a rise in temperature. On the other hand, maleic acid, fumaric acid and dihydroxybenzene decrease with a rise in temperature. Since the oxidation of maleic acid gives acetaldehyde, formaldehyde, and acetic acid, these products are considered to be produced through maleic acid from phenol. However, acetone is not given from maleic acid, but from phenol.

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[8] E. Bernatek and K. A. Sraumsgård, *Acta Chem. Scand.*, **13**, 178 (1959).

[9] E. Bernatek and C. Frengen, ibid., **15**, 471 (1961).

[10] E. Bernatek, J. Møkleland and K. Valen, ibid., **15**, 1454 (1961).