The Thermal and Radiation Oxidation of Benzene to Phenol in Aqueous Solutions Containing Metal Ions at Elevated Temperatures. IV. The Effect of Impurities in Benzene

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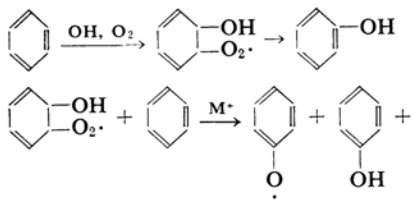
The oxidation of benzene to phenol catalyzed by metal ions has been studied in aqueous solutions under high oxygen pressure at elevated temperatures.[1,2] In a ferrous sulfate solution, phenol is produced in a good yield either with or without gamma-ray irradiation.[1] In a ferric sulfate solution, phenol is similarly produced by irradiation, but only above 180°C when not irradiated.[1] In a cupric sulfate solution, phenol is produced above 180°C either with or without irradiation.[2]

These facts have been interpreted as follows:[1,2] The chain processes of benzene oxidation are:

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).



(1)

(2)

$$PhO + PhH = PhOH + Ph \quad (3)$$

$$Ph + O_2 = PhO_2 \quad (4)$$

$$PhO_2 + PhH = PhO_2H + Ph \quad (5)$$

$$PhO_2H + M^{2+} = PhO_2 + H^+ + M^+ \quad (6)$$

$$PhO_2H + M^+ = PhO + OH^- + M^{2+} \quad (7)$$

$$2PhO_2 = 2PhO + O_2 \quad (8)$$

where Ph represents the phenyl radical, M^+, the ferrous or cuprous ion, and M^{2+}, the ferric or cupric ion. The OH radicals for the initiation reaction 1 are produced from the reactions:

$$H_2O \rightsquigarrow H, OH, H_2, H_2O_2 \quad (9)$$

$$M^+ + O_2 + H^+ = M^{2+} + HO_2 \quad (10)$$

$$HO_2 \text{ or } H_2O_2 \xrightarrow{M^+} OH \quad (11)$$

However, the phenol production above 180°C in non-irradiated ferric or cupric solutions cannot be interpreted in terms of the above reaction scheme because of a lack of reactions 9, 10 and 11. This fact suggests that there are some additional reactions above 180°C. Later, it has been found, as is shown in the present paper, that the results for carefully purified benzene are quite different from the previous results.[1,2] These observation will be interpreted in the present paper, together with the effect of impurities in benzene.

Experimental

Benzene was purified carefully by several methods, using mercury, sulfuric acid, sodium hydroxide, freezing, and distillation. The concentration of impurities in benzene with and without purification, analyzed by gas chromatography, using TCP-column at 70°C, is shown in Table I. Cyclohexane could not be separated by the present methods.

Benzene, with or without purification, was oxidized in neutral aqueous solutions of ferrous, ferric and cupric sulfates,[3] by means of the following procedure, as in the previous paper:[1] 1 cc. of benzene was put on 15 cc. of the aqueous phase in a hard-glass tube in a 50 cc. stainless-steel reactor under the oxygen pressure of 30 atm. Then this system was heated by a controlled procedure and kept for 30 min. at a given temperature. When it was irradiated, the dose was about 1.3×10^4 r of cobalt-60 gamma-rays for 25 min.

After cooling, it was analyzed by the same methods as in the previous papers.[1,2] A large portion of the iron species was precipitated above 160°C.

3) The initial concentration of metal ions was 0.01 M, except for the experiments shown in Fig. 4 and Table II.

Results and Discussion

The Ferrous Sulfate Solution. — The total amounts of phenol produced in the solution of 0.01 M ferrous, ferric and cupric sulfates[3] with (circle marks) and without (triangle marks) radiation are plotted against the reaction temperature in Figs. 1, 2 and 3 in order to compare purified (solid marks) and unpurified (open marks) benzene.

The yield of phenol from unpurified benzene is larger than that from purified benzene, even in the ferrous solution. This indicates that some peroxides are forced rseadily to initiae the chain process from the impurities in unpurified benzene, which is more readily oxidized than benzene. That is, the reaction

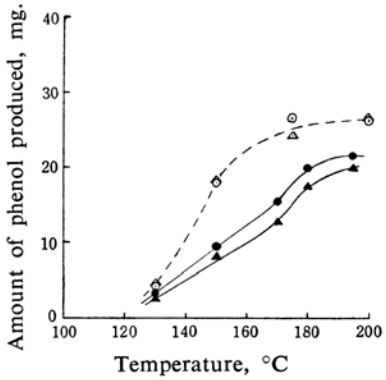


Fig. 1. Amounts of phenol produced in the irradiated (⊙ and ●) and non-irradiated (△ and ▲) neutral 0.01 M ferrous sulfate solutions, from purified (solid marks) and unpurified (open marks) benzene.

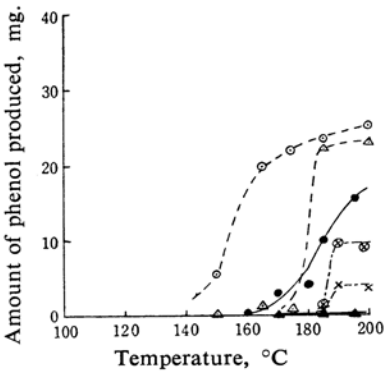


Fig. 2. Amounts of phenol produced in the neutral 0.01 M ferric sulfate solutions; circle and triangle marks are the same as in Fig. 1. The results in the non-irradiated solution for purified benzene containing toluene (3.3×10^{-3} M) and thiophene (4×10^{-4} M) are shown by ⊗ and × respectively.

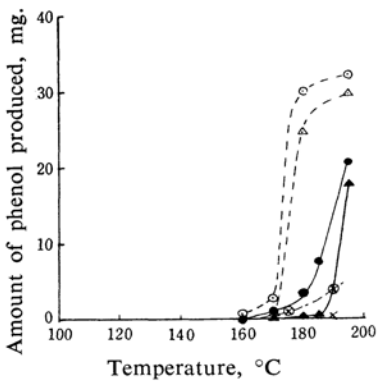


Fig. 3. Amounts of phenol produced in the neutral 0.01 M cupric sulfate solution; circle and triangle marks are the same as in Fig. 1. The results for purified benzene in the 0.01 M cupric sulfate—0.01 M ferric sulfate solution are show by ⊗ and × for the irradiated and non-irradiated cases respectively.

$$RH \xrightarrow{OH,\ O_2} \text{peroxide } (R'O_2) \qquad (12)$$

(RH: impurities in benzene)

should be assummed to be a faster initiation process than reaction 1 for cases of unpurified benzene. R′ is not necessarily equal to R. It is known that a small of organic additives promotes the oxidation of benzene to phenol in the gaseous phase.[4]

The results in the ferrous sulfate solution, seen in Fig. 1, can be interpreted by means of the present reaction scheme.

The Irradiated Ferric Sulfate Solution.—The results in the irradiated ferric sulfate solution, shown by open and solid circles in Fig. 2, can also be interpreted by means of reaction 12. The remarkable decrease in the phenol yield upon purification indicates that the initiation process is reaction 12 rather than reaction 1. Even for purified benzene, the chain process might be initiated by the oxidation of cylohexane, which cannot be separated by the purification described previuosly. Accoring to Bach,[5] the yield of radiation oxidation is in the order of *n*-heptane>toluene>cyclohexane> benzene. Therefore, reactions 13—15:

$$R'O_2 + PhH = R'O_2H + Ph \qquad (13)$$

$$R'O_2H + M^{2+} = R'O_2 + H^+ + M^+ \qquad (14)$$

$$R'O_2H + M^+ = R'O + OH^- + M^{2+} \qquad (15)$$

should form the initial process instead of reactions 1 and 2. Phenyl radicals are consumed as in the previous scheme. Hydroxycyclohexadienyl peroxide, detected by Dorfman et al,[6] may not take a major part in the chain process at elevated temperatures; it does only as a precursor to phenol, as is shown in reaction 1. The greater part of the OH radicals from reactions 9, 10 and 11 are consumed by reaction 12 rather than by reaction 1, at least at the initial stage. The rate of the chromic acid oxidation of benzene is very slow in comparison with that of other compounds.[7]

When there are a large number of ferrous ions, as in the ferrous solution, reaction 2 may play some part in the initiation process (see Fig. 1). At any rate, it is certain that ferrous ions are indispensable to the chain process at lower temperatures in either reaction 2 or 12, for scarcely any phenol is produced below 160°C from purified benzene in Fig. 2, even when it is irradiated. It may also be concluded from a comparison of the results of purified benzene in the irradiated ferrous and in the same ferric solutions that the yield of OH radicals by in reaction 10 is much larger than that by reaction 9.

Since almost all of the iron species are ferrous in the solution after oxidation reaction, it is supposed that the rate of reaction 6 is faster than that of reaction 7. As phenyl peroxides are accumulated by reaction 6, they are converted to phenoxy radicals for reaction 3 by reaction 8.

Only a small amount of phenol is produced, even from unpurified benzene, at 200°C in an irradiated aqueous phase containing no metal ions, as is shown in Table I of Part II.[1] This is due to the lack of reactions 14 and 15, which regenerate $R'O_2$ and R′O.

The Non-irradiated Ferric Sulfate Solution.—As shown by open and solid triangles in Fig. 2, in the non-irradiated ferric sulfate solution, phenol is produced in a good yield above 180°C from unpurified benzene in spite of the lack of reactions 9, 10 and 11 to give OH radicals for reaction 12. On the other hand, purified benzene is hardly oxidized to phenol at least up to 200°C. Therefore, the initiation process for this case is attributed to the formation of hydroperoxides by oxygen from the impurities:

$$RH \xrightarrow{O_2} RO_2H \qquad (16)$$

The hydroperoxides are isolated for the oxiation of the compounds listed in Table I.[8,9] Since the hydroperoxides are built up to some

4) W. I. Denton, H. G. Doherty and R. H. Krieble, *Ind. Eng. Chem.*, **42**, 777 (1950).
5) N. Bach, *Proc. Intern. Conf. of Geneva*, **7**, 538 (1956).
6) L. M. Dorfman, I. A. Taub and R. E. Bühler, *J. Chem. Phys.*, **36**, 3051 (1962).
7) F. Mares and J. Rocek, *Collection Czechoslov. Chem. Commun.*, **26**, 2370 (1961).
8) C. Walling, "Free Radicals in Solution," John Wiley & Sons, New York (1957), Chap. 9.
9) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, New York (1954).

TABLE I. IMPURITY CONCENTRATIONS AND THEIR EFFECT

Impurity	Concn., M		Yield of phenol, mg.[a]	
	before purification	after purification	I[b]	II[c]
Carbon disulfide	4×10^{-4}	0	3.6	3.6
n-Hexane	4×10^{-4}	0	1.1	1.1
Cyclohexane	6.7×10^{-3}	6×10^{-3}	0.1	<0.1
Cyclohexene	$<2 \times 10^{-5}$e	0	0.4[d]	2.5
Thiophene	$<6 \times 10^{-4}$e	0	3.1[d]	3.0
Toluene	3.3×10^{-3}	0	9.9	3.4
Xylene	0	0	—	—

Note:

a) The amount of phenol produced at 190°C in the non-irradiated neutral ferric sulfate solution.
b) For benzene containing the same amount of the respective impurity as unpurified benzene.
c) For benzene containing 4×10^{-4} M of the respective impuritiy.
d) For benzene containing the amount of the upper limit before purification, noted by e, as an impurity.

extent above 180°C, they can propagate the chain process, as has been mentioned with regard to reaction 12. The rate of reaction 12 must be larger than that of reaction 16, especially at temperatures lower than 170°C, in view of the difference in unpurified benzene with and without irradiation.

To compare the relative promotive effect of the respective impurities, they were added separately, in portions as large as are present in unpurified benzene, to purified benzene. The amounts of phenol produced from this benzene at 190°C are shown in column I of Table I. The effect of toluene (3.3×10^{-3} M, ⊗) and thiophene (4×10^{-4} M, ×) were examined at other temperatures also, as Fig. 2 shows. Moreover, they are compared by adding an equal amount of 4×10^{-4} M, as is shown also in column II of Table I.

Although cyclohexane seems not, judging from Table I, to promote the production of phenol, its hydroperoxide is also actually isolated.[8] Therefore, a small amount of phenol production for non-irradiated purified benzene, as is seen in Fig. 2, may be attributed not to a trace amount of ferrous ions in the ferric solution, as was assumed in Part II,[1] but to cyclohexane as an impurity.

The Cupric Sulfate Solution.—All the results for the 0.01 M cupric sulfate solution, shown by circles and triangles in Fig. 3, are consistent with the above conclusions.

For the results of unpurified benzene, it is noticeable that the tendency is almost the same in the non-irradiated solution as for ferric sulfate, seemingly supporting reaction 16 as the common process. The lack of the production of phenol below 160°C for the irradiated case is attributed to the lack of cuprous ions because of the fast rate of cuprous oxidation if it is produced, as has been discussed in Part III.[2] On the other hand, phenol is produced in a good yield above 180°C. This is due to the build-up of indispensable cuprous ions over cuprous oxidation with the rise in temperature, which accelerates not only the formation of hydroperoxides but also their thermal decomposition by cupric ions.

Phenol is produced remarkably well at 200°C from purified benzene, even in the non-irradiated solution, in contrast to the case of ferric sulfate. This is due to the difference between the ion concentrations in the solution; that is, hardly any cupric sulfate is precipitated, even at 200°C, but ferric sulfate is almost all precipitated, up to less than 10^{-4} M. In fact, the yield of phenol decreases with a decrease in the cupric concentration, as is shown in Fig. 4, which gives the results of purified benzene in the non-irradiated aqueous

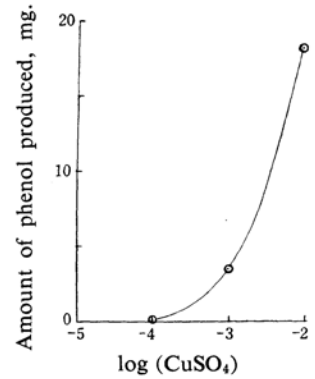


Fig. 4. Amount of phenol produced at 198°C purified benzene in the non-irradiated aqueous solution as a function of the concentration of cupric sulfate in M.

TABLE II. DEPENDENCE OF SULFATE CONCENTRATION

Composition of aq. soln., M				Amount of phenol produced (198°C) mg.	Ferrous concentration after reaction M
$CuSO_4$	$Fe_2(SO_4)_3$	Na_2SO_4	Total SO_4		
0.001	0	0	0.001	3.52	—
0.001	0.00005	0	0.00115	4.08	5.3×10^{-5}
0.001	0.0005	0	0.0025	1.50	5.1×10^{-5}
0.001	0	0.0015	0.0025	1.68	—
0.001	0.005	0	0.016	0.24	6.6×10^{-5}
0.001	0	0.015	0.016	0.50	—

solution of cupric sulfate. Such dependence of the cupric concentration was reported for unpurified benzene by Terakawa et al.[10]

The Cupric-Ferric Sulfate Solution.—As is shown in Fig. 3, the yield of phenol decreases in the irradiated (⊗) and non-irradiated (×) cupric sulfate solutions when 0.01 M ferric sulfate is added. The same fact is also shown for unpurified benzene in Fig. 3 of Part III.[2] For these cases, the concentration of iron species is no mere than 10^{-4} M at elevated temperatures due to precipitation, but the greater part of sulfate groups are still in the solution. On the other hand, the yield of phenol is suppressed in the concentrated sulfuric acid solution, as is seen in Fig. 1 of Part III.[2] This decrease in the yield is supposed to be attributable to the decrease in the cupric ion concentration due to the suppression of the dissociation of cupric sulfate effected by the addition of sulfate groups. To confirm this assumption, purified benzene was oxidized at 198°C without radiation in an aqueous solution of 0.001 M cupric sulfate by adding various amounts of ferric or sodium sulfate so as to give the equivalent sulfate concentration for both cases. The results, shown in Table II, indicate that the amounts of phenol produced are dependent on the total concentration of sulfate, but are independent of the kind of cation apparently supporting the above assumption.

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

Summary

The yield of phenol from the oxidation of unpurified benzene catalyzed by metal ions in an aqueous solution is much larger than from that of purified benzene. Phenol is produced in a good yield at temperatures lower than 160°C only in an oxygenated solution, in which OH radicals are produced, either with or without irradiation. Therefore, the autoxidation of impurities in benzene, initiated by OH radicals, is the initiation reaction of the chain oxidation process. On the other hand, phenol is also produce above 180°C even when OH radicals are not produced. Therefore, it is considered that the hydroperoxides of impurities are formed at higher temperatures without the OH radical by means of their autoxidation. Moreover, the yield of phenol in a cupric sulfate solution decreases remarkably with an increase in the sulfate concentration.

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