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Thermal and Radiation Oxidations of Benzene to Phenol in Aqueous Solutions Containing Metal Ions at Elevated Temperatures. VII. The Mechanisms of Phenol Formation as Studied by Stable Isotopes*

By Hiroshi HOTTA, Nobutake SUZUKI and Toshihiko ABE

Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute, Takasaki, Gunma

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When benzene was oxidized to phenol in an oxygen-18 enriched aqueous solution of iron and copper sulfates, the oxygen-18 was much concentrated to phenol. The oxygen-18 content depended on the kind of metal ion and on the temperature. This suggests that the oxygen in the phenol produced is donated not only by the molecular oxygen, but also by the water. Therefore, it is assumed for the termination process that phenol is formed by the ionic reactions. Furthermore, when an equimolar mixture of benzene and benzene-d_6 was oxidized, the isotope effect of hydrogen, k_H/k_D, as estimated from the isotopic composition of the phenol produced, was about 1.2. This value seems to be small for the hydrogen abstraction reaction of radicals. Therefore, when we compare these results with the other facts reported previously, the main reaction of the propagation process may be supposed to be the abstraction reaction of hydrogen by phenyl peroxide. In this experiment, it was also found that phenol exchanges hydrogen with water. The rate constant of the exchange reaction was estimated by Bateman's equation. The rate constant is the highest in the ferric sulfate solution.

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The effects of metal ions on the autoxidation of benzene to phenol in aqueous solutions of iron and copper sulfates have previously been studied in our laboratory.[1-6] The present paper will describe the results of the studies which were carried out by using stable isotopes, i. e., oxygen-18 enriched water, benzene-d_6 and deuterium oxide, in order to confirm the reaction scheme hitherto assumed. The reactions in the oxygen-18 enriched water solution other than phenol formation will be discussed in the following paper, also in this Bulletin.

Experimental

Oxidation Procedure.—Benzene was oxidized in oxygen-18 enriched aqueous solutions of ferrous, ferric and cupric sulfates by the following procedure, described in a previous paper.[2] These sulfate solutions were prepared by dissolving 0.01 M of metal ion.[1] Oxygen-18 enriched water (1.63 oxygen-18 atom %) was obtained from the Weizman Institute of Science, Israel.

One cubic centimeter of benzene was put on 15 cc. of the aqueous phase in a hard-glass tube in a 50 cc. stainless-steel reactor under an oxygen pressure of 30 atm. This system was then heated by a controlled procedure and kept 30 min. at a given temperature. When it was irradiated, a dose of about 13000 r. of cobalt-60 gamma rays was given for 25 min. Some related experiments were also carried out under other conditions for the sake of reference.

The Analysis of Oxygen-18 in Phenol.—Phenol was separated into 30 cc. of water after ether extraction from the above aqueous phase. It was precipitated as tribromophenol by adding 50 cc. of a 0.1 N bromide solution, a solution of potassium bromate and potassium bromide, and 10 cc. of 12 N hydrogen chloride. The precipitate was purified by sublimation at 100°C using the suction of an aspirator. The oxygen-18 content was analyzed using a mass spectrometer according to the method of Rittenburg and Ponticorvo.[7]

The Experiment on Benzene-d_6.—In order to study the isotope effect of hydrogen at the above oxidation, benzene-d_6 (Merck Sharp & Dohme of Canada, Ltd.) was mixed with benzene in the ratio, $C_6H_6 : C_6D_6 : C_6HD_5 : C_6H_2D_4 : C_6H_3D_3 : C_6H_4D_2 : C_6H_5D = 100 : 93.7 : 4.1 : 0.4 : 0.4 : 0.1 : 0.1 : 0.0$, according to mass spectrometry.[8] This benzene mixture was then oxidized in the solutions of natural water by the above oxidation procedure. This ratio did not change for the unreacted benzene within the range of experimental error after oxidation in the present degree of conversion.

After the phenol produced, which was extracted into ether by the previous method,[2] had been separated by gas chromatographic fractionation using the columm of PEG 6000 at 170°C, the abundance ratio between various deuterated phenols in the product (cf. Table III) was determined from the mass spectrum on the following assumption. That is, the ion abundance ratio between $C_6H_5O^+$, $C_6H_5OH^+$ and $^{12}C_5{}^{13}CH_5OH^+$ for the mass spectrum of phenol is 2.06 : 100 : 6.69. Since the formation of these ions is independent of hydrogens of the benzene ring, the ratio between $i-1$., i and $i+1$'th peaks ($i=m/e$ of parent peak) is assumed to be the same for the mass spectrum of various deuterated phenols.

Benzene was also oxidized in the solution of deuterium oxide (99.75%, Showa Denko Co., Tokyo) by the same procedure.

Results

Oxygen-18 in Phenol.—Since the previous papers[1-6] have shown that the yield of phenol in

TABLE I. ATOM-% OF OXYGEN-18 IN PHENOL PRODUCED AT BENZENE OXIDATION

No.	Additive	Temp., °C	Atom-% of ^{18}O	Oxygen of phenol from water, F_w, %[d]	Ref.
1	$FeSO_4$	150	0.48	19	2
2	$FeSO_4$	180	0.99	55	2
3[a]	$FeSO_4$	180	0.90	49	2
4[b]	$FeSO_4$	180	0.90	49	4
5	$FeSO_4$	200	0.88	46	2
6	$Fe_2(SO_4)_3$	180	0.93	51	2
7[a]	$Fe_2(SO_4)_3$	180	1.06	60	2
8	$CuSO_4$	200	0.62	30	3
9[a]	$CuSO_4$	200	0.61	29	3
10[b]	$CuSO_4$	200	0.76	39	4
11[b]	$CuSO_4$+Cu-pieces	200	0.53	23	3
12[b]	Cu-pieces	200	0.48	19	3
13[c]	$CuSO_4$	200	0.44	15	4

a) Irradiated run b) Using purified benzene c) The 0.001 M $CuSO_4$ solution
d) Estimated from Eq. i

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[1] H. Hotta and N. Suzuki, This Bulletin, **36**, 717 (1963).

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

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

[4] N. Suzuki and H. Hotta, ibid., **37**, 244 (1964).

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

[6] H. Hotta, N. Suzuki, N. Itatani, K. Shimada, ibid., **37**, 1147 (1964).

[7] D. Rittenburg and L. Ponticorvo, *J. Appl. Rad. Isotopes*, **1**, 208 (1956).

[8] API Mass Spectral Data, Series No. 609, Carnegie Inst. Techn., Pittsburgh (1956).

the oxidation of benzene depends on the kind of metal ions, the impurities in the benzene, irradiation with gamma rays, and so on, the atom percentage of oxygen-18 in the phenol produced was examined in oxygen-18 enriched aqueous solutions at the various conditions listed in Table I. Experiments 3, 7 and 9 were carried out with gamma-ray irradiation. The purified benzene was used for experiments 4, 10, 11 and 12. The purity of the benzene used for the other experiments was the same as was shown in Table I of Part VI.[6] Two grams of copper pieces were added for experiments 11 and 12. Experiment 13 was carried out in an aqueous solution of 0.001 M cupric sulfate. The significance of these conditions is described in the previous paper referred to the last columm of Table I.

For reference, the aqueous solutions of phenol (0.021 M) were also treated by the same procedure as was used in the benzene oxidation under the pressure of either oxygen or nitrogen (30 atm. at 20°C). The results, shown in Table II, show that the content of oxygen-18 in phenol is not changed by the present procedure.

Therefore, the increase in oxygen-18 in Table I is not due to the exchange reaction of oxygen between water and the phenol produced, but to some reaction in the oxidation process of benzene.

TABLE II. ATOM-% OF OXYGEN-18 IN TREATED PHENOL

No.	Additive	Temp. °C	Atmosphere[a]	Atom-% of ^{18}O
14	None	180	Oxygen	0.21
15	$FeSO_4$	180	Nitrogen	0.21
16	$Fe_2(SO_4)_3$	180	Nitrogen	0.20
17	$Fe_2(SO_4)_3$	180	Oxygen	0.21

a) 30 atm. at 25°C.

This means that some part of the oxygen in the phenol produced does not come from gaseous oxygen but from water during the phenol formation. The percentage of such oxygen given from water, F_w, is estimated by the equation:

$$F_w=\frac{(x-0.20)}{(1.63-0.20)}\times 100 \tag{i}$$

as is shown in Table I, where x is the observed value of the atom percentage of oxygen-18 in phenol.

When the results are compared, it may be concluded that 52±3% of oxygen are transferred from water to phenol at 180°C in an aqueous solution of iron sulfates, regardless of ferrous or ferric sulfate, purification of benzene, and irradiation, and that the corresponding percentage is 33±5% at 200°C in an aqueous solution of cupric sulfate.

TABLE III. DEUTERIUM DISTRIBUTION IN PHENOL

No.	20	21	22	23	24	25	26	27	28	28	30
Reactant	$C_6H_6+C_6D_6$	$C_6H_6+C_6D_6$	$C_6H_6+C_6D_6$	C_6H_6	C_6H_6	C_6H_6	C_6H_6	C_6H_5OH	C_6H_5OH	C_6H_5OH	C_6H_5OH
Additive	$FeSO_4$	$FeSO_4$	$CuSO_4$	$FeSO_4$	$FeSO_4$	$Fe_2(SO_4)_3$	$CuSO_4$	$FeSO_4$	$FeSO_4$	$Fe_2(SO_4)_3$	$CuSO_4$
Medium	H_2O	H_2O	H_2O	D_2O	D_2O	D_2O	D_2O	D_2O	D_2O	D_2O	D_2O
Temp., °C	150	180	200	150	180	200	200	150	180	200	200
Ratio of products											
C_6H_5OH	100	100	100	100	100	100	100	100	100	100	100
C_6H_4DOH	3.9	2.3	2.4	15.8	77.1	66.8	38.7	4.0	51.0	401.7	46.2
$C_6H_3D_2OH$	1.4	4.0	0.8	2.7	61.4	108.1	12.5	0.6	13.4	724.3	11.6
$C_6H_2D_3OH$	2.1	15.0	2.8	0.4	25.2	408.5	3.3	0.5	1.8	457.9	2.0
C_6HD_4HOH / C_6HD_4OH	13.2	26.8	16.3	0.0	2.0	40.8	0.3	0.4	0.1	38.0	0.1
C_6D_5OH	62.5	29.3	62.9	0.0	0.2	2.7	0.1	0.0	0.1	2.7	0.0
Total of d-phenols	83.1	77.4	85.2	18.9	165.9	626.9	54.9	5.5	66.4	1624.6	59.9
k_H/k_D	1.19	1.28	1.16	—	—	—	—	—	—	—	—

When experiments 1 and 13 are compared with others, it may be seen that the value of F_w increases with the temperature and with the concentration of metal ions.

Deuterium Distribution in Phenol.—Under the conditions shown in Table III, the benzene mixed with deuterated benzene was oxidized in natural water (experiments 20—32), while benzene without deuterated benzene was oxidized in deuterium oxide (experiments 23—26). For reference, the solution of phenol in deuterium oxide was also treated by the same procedure as was used for the benzene oxidation.

After experimentation, the abundance ratios between various deuterated phenol were determined as to be shown in Table III by the procedure mentioned above. The ratios in experiments 20—22 are quite different from the original benzene mixture. Such deuterium transfer appears to be independent of the oxidation process of benzene, for it also occurs to a considerable extent in the solution of phenol, as is shown for experiments 27—30. The hydroxyl group of phenol formed in deuterium oxide was changed to OH-group during separation of phenol from the aqueous solution, even if it was OD-group (experiments 23—30).

Discussion

Oxygen of the Hydroxyl Group.—It has been assumed that the present autoxidation of benzene is propagated by the abstraction of the hydrogen atom from benzene (reaction 3) as follows:

$$RO_2 + PhH = RO_2H + Ph\cdot \tag{1}$$

$$Ph\cdot + O_2 = PhO_2 \tag{2}$$

$$PhO_2 + PhH = PhO_2H + Ph\cdot \tag{3}$$

$$PhO_2H + M^+ = PhO\cdot + OH^- + M^{2+} \tag{4}$$

$$PhO_2H + M^{2+} = PhO_2 + H^+ + M^+ \tag{5}$$

$$2PhO_2 = 2PhO\cdot + O_2 \tag{6}$$

where M^+ represents a ferrous or cuprous ion, and M^{2+}, a ferric or cupric ion. The initiation process of the peroxide formation (RO_2) is omitted in the present paper.[4]

However, it is not explained in the above reaction scheme how to form phenol from the phenoxy radicals accumulated. The process for it can be interpreted on the basis of the present finding in Table I, by taking the ionic reaction scheme as follows[9,10]:

$$PhO\cdot + M^+ = PhO^{-}\cdot + M^{2+} \tag{7}$$

$$PhO^{-}\cdot + H^+ = PhOH \tag{8}$$

and

$$PhO_2 + M^{2+} = Ph^{+}\cdot + O_2 + M^+ \tag{9}$$

$$Ph^{+}\cdot + O^{*}H^- = PhO^{*}H \tag{10}$$

where O* is the oxygen atom from water. The values of F_w in Table I obtained from Eq. i can be interpreted as the result of the competition between reactions 4 and 7 and reactions 5 and 9.

Benzene is not oxidized to phenol in the cupric sulfate solution, even with irradiation at temperatures lower than 180°C, because cuprous ions are immediately oxidized by oxygen if produced by reaction 5.[3,4] The fact suggests that, in the above reaction scheme, the rate of reaction 9 is extremely slow at the lower temperature, because phenol is not formed by the aid of cupric ions, and because reaction 7, another path of phenol formation, can not occur due to the lack of cuprous ions. On the other hand, a considerable amount of phenol is produced at 200°C.[3,4] Therefore, it may be supposed that the rate of reaction 5 is so fast at 200°C that a larger amount of cuprous ions is produced than is consumed by their oxidation. The low value of F_w in Table I suggests that the rate of reaction 9 becomes significant at 200°C, but that it is not so fast as for iron ion to be discussed below.

Since ferrous ions are not oxidized as quickly as cuprous ions,[1] phenol is produced by reaction 7 in the iron sulfate solutions.[2,4] Since the values of F_w in Table I increase between 150°C and 180°C, the rate of reaction 9 is sure to increase in this temtemperature range. This is consistent with the above assumption that the rate of reaction 9 for cupric ions is very dependent on temperature in the same range. Almost all the iron species are ferrous in solutions after the oxidation of benzene.[2] This accumulation of ferrous species is due to the fast rate of reaction 5 and the slow oxidation of ferrous ions rather than to the fast rate of reaction 9. Phenyl peroxides, accumulated by reactions 3 and 5, might be converted to phenoxy radicals by reaction 6, and then to phenol by reaction 7. Therefore, it may be concluded that phenol is mainly produced by reaction 4—7, not by reaction 9, at least at lower temperatures.

The oxygen-18 content in the phenol produced in Table I, is larger in iron sulfate solutions than in a 0.01 M cupric sulfate solution as well as in a 0.001 M cupric sulfate solution. The concentration of iron species in iron sulfate solutions at 180°C (experiments 2, 3, 4, 6 and 7) is about 0.0002 M due to the precipitation of ferric oxides.[1,2] This means that iron ions are much more reactive than copper ions in the present process, and that the rate of reaction 9 for ferric ions is quite different from that for cupric ions.

Recently, Vysotskaya reported that the phenol which was produced by hydrogen peroxide in the presence of ferrous or ferric ions in oxygen-18 enriched water contained some of oxygen-18.[11] Although this is of much interest in relation to the

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[9] A. V. Tobolosky and R. S. Mesrobian, "Organic Peroxides," Interscience Publ., New York (1954), p. 103.

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

[11] N. A. Vysotskaya, *Zh. Fis. Khim.*, **38**, 1688 (1964).

present study, it must be noted that phenol is produced through the non-chain process at room temperature, not through the chain process as in the present study.

The Isotope Effect of Hydrogen on Benzene Oxidation.—The isotope effect of hydrogen on the oxidation of deuterated benzene might prove the abstraction reaction of the hydrogen atom from benzene by a free radical (reaction 3), because the reactions above-mentioned scheme are independent of the dueterium atom except reaction 3. For this purpose, since the conversion of benzene is very low in the present study, the rate-constant ratio, k_H/k_D, is estimated for experiments 20—22 in Table III by the equation:

$$\frac{k_H}{k_D}=\frac{(C_6H_5OH)}{(C_6H_6)}\times\frac{\sum\limits_{i=1}^{5}(C_6H_iD_{6-i})}{\sum\limits_{i=1}^{4}(C_6H_iD_{5-i}OH)} \qquad \text{(ii)}$$

Although the isotope effect or the rate-constant ratio, k_H/k_D, is usually larger than the values in Table III, i. e., about 1.2, for the hydrogen abstraction reaction by free radicals, the reactions with the smaller activation energy have the smaller isotope effect.[12] The rate of the autoxidations is mainly controlled by the rate of the abstraction reaction by peroxides, as in reaction 3. However, it is very difficult in the present system to obtain an activation energy which is physically meaningful, due to the complexity of the pre-equilibration between reactants related to the reaction in question. At any rate, the temperature-dependent coefficient apparently corresponds to about 10 kcal./mol. between 150°C and 180°C for the oxidation of purified benzene in the aqueous solution of ferrous sulfate, judging from the result reported previously.[4] The value obtained by Terakawa et al. is 6 kcal./mol.[13] Both values are smaller than the value for the autoxidation of parrafins, 15 kcal./mol.[14]

It is confirmed that the formation of phenol in the aqueous solution of benzene at room temperature, by radiation and the Fenton's reagent, is to be attributed to the addition reaction of the hydroxyl radical.[15,16] On the other hand, the present chain autoxidation of benzene at elevated temperatures cannot be understood by the same mechanisms due to the following facts. a) No ferric ions are reduced in the mechanisms of the Fenton's reagent, but almost all the iron species are ferrous after the present experimentation.[2] Especially, in the presence of oxygen, it is very difficult to see how ferric ions are reduced. b) The yield of phenol increases abruptly above 170°C.[4] This fact cannot be interpreted without assumption of reactions 1 and 3, because the yield of the hydroxyl radical cannot increase like the yield of phenol. c) The effect of the impurities in benzene indicates that the initiation of the present process is not the direct reaction between benzene and hydroxyl radical.[4] Therefore, reaction 1 must be assumed at first for the oxidation of benzene.

The Exchange Reaction of Hydrogen.—As has already been shown in the section on "Results," the isotopic composition of the phenol produced in Table III is quite different from that of the original benzene mixture. This is due to the exchange reaction of hydrogen between phenol and water, which is independent of the oxidation process of benzene.

Phenol makes phenolate with ferric ions, not with ferrous or cupric ions, so phenol is usually analyzed qualitatively as ferric phenolate. It has been reported that phenol in deuterium oxide exchanges the hydrogen atom of *o*- and *p*-positions only and hydroxyl group with water.[17] On the other hand, in Table III, the exchange of the hydrogen atom is extremely high in the ferric sulfate solution (experiments 28—30), and the phenol having more than three deuterium atoms is very little. Therefore, it may be concluded that the formation of a Ph-O-M bond (M=metal ion) induces the hydrogen exchange of the *o*- and *p*-positions electronically.

Since the exchange reaction of hydrogen is consecutive, as in:

$$\begin{array}{ccccc} C_6H_5OH & \xrightarrow[k_1]{} & C_6H_4DOH & \xrightarrow[k_2]{} & C_6H_3D_2OH \\ (N_1) & & (N_2) & & (N_3) \\ & \xrightarrow[k_3]{} & C_6H_2D_3OH & \xrightarrow[k_4]{} & \\ & & (N_4) & & \end{array} \qquad (11)$$

the rate constant of the exchange reaction for the i'th deuterium atom, k_i, can be estimated by Bateman's equation[18]:

$$N_1=N_{01}e^{-k_1t} \qquad \text{(iii)}$$

$$\frac{N_i}{N_{01}}=\frac{k_1k_2k_3\cdots k_{i-1}}{(k_2-k_1)(k_3-k_1)(k_4-k_1)\cdots(k_i-k_1)}e^{-k_1t} + \frac{k_1k_2k_3\cdots k_{i-1}}{(k_1-k_2)(k_3-k_2)\cdots(k_i-k_2)}e^{-k_2t}+\cdots + \frac{k_1k_2k_3\cdots k_{i-1}}{(k_1-k_i)(k_2-k_i)\cdots(k_{i-1}-k_i)}e^{-k_it} \qquad \text{(iv)}$$

where N_i is the number of phenol molecules attacked by the i'th deuterium atom at time $t=t$, which is N_{01} at $t=0$.

The rate constants shown in Table IV are

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12) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

13) A. Terakawa, Y. Hosaki, M. Nitto and T. Hirayama, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **66**, 80 (1963).

14) G. H. Twigg, *Chem. Eng. Sci.*, **1954**, 3 Spec. Suppl., 5.

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

16) J. R. L. Smith and R. O. C. Norman, *J. Chem. Soc.*, **1963**, 2897.

17) A. Murry and D. L. Williams, "Organic Syntheses with Isotopes," Part II, Interscience Publ., New York (1958), p. 1652.

18) H. Bateman, *Proc. Cambridge Phil. Soc.*, **15**, 423 (1910).

estimated for experiments 27—30 by the above equations from the observed values listed in Table III on the assumption that the reaction time, t, is 1800 sec. Since the true time should be longer than this time because of some contribution of the reaction during heating and cooling,[1,2] the corrected rate constants would be faster than the present values. This increase would be ten percent at most. Furthermore, since the sulfate solutions containing benzene or phenol become a ferrous and ferric mixture at elevated temperatures, regardless of whether they are ferrous or ferric originally,[2,5] the true rate should be faster for ferric ions and slower for ferrous ions than the present values. For the cupric sulfate solution, the contribution of cuprous ions can be ignored because of their fast autoxidation.[3]

In comparing the rate constants in Table IV, it can be seen that the first rate constants, k_1, are not very different from the second rate constants, k_2, but are larger than the third rate constants, k_3. However, the accuracy of the third rate constants is the lowest.

TABLE IV. RATE CONSTANTS OF EXCHANGE REACTION OF HYDROGEN IN sec^{-1}

No.	27	28	29	30
k_1	2.97×10^{-5}	2.83×10^{-4}	1.58×10^{-3}	2.57×10^{-4}
k_2	3.00×10^{-5}	2.60×10^{-4}	1.20×10^{-3}	2.58×10^{-4}
k_3	1.70×10^{-5}	1.35×10^{-4}	0.65×10^{-3}	2.49×10^{-4}

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