Thermal and Radiation Oxidations of Benzene to Phenol in Aqueous Solutions Containing Metal Ions at Elevated Temperatures. II. The Effect of Iron Sulfate and Chloride on Phenol Yield

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The yield of phenol in the thermal oxidation of gaseous benzene has been reported to be at its optimum at about 400°C in the presence of some organic promotors[2,3]. The thermal oxidation of benzene to phenol has usually been made at temperatures higher than 300°C, giving some amount of biphenyl as by-product.

As mentioned in the introduction to Part I of the present series[4], it is expected that benzene can be also oxidized to phenol with a good yield in the aqueous phase at lower temperatures by the use of cobalt-60 gamma rays. However, the irradiation method without metal salt also gives some amount of biphenyl[5]. On the other hand, it is well known that oxidation reaction is usually promoted in the presence of metal ions[6,7]. In fact, benzene is oxidized to phenol without biphenyl production in the presence of iron salts at temperatures lower than 200°C as is shown in the present paper.

Experimental

Apparatus and Procedure.—1 ml. of benzene, purified by the usual method, was put on 15 ml. of an aqueous solution of 0.01 M iron ion, as has been mentioned in Part I[4], in a hard-glass tube in the reactor under the oxygen pressure of 30 atm. This system was heated by the controlled procedure mentioned in Part I. Although the reactor had no stirring device, the solution seemed to be agitated spontaneously at elevated temperatures, at least above 150°C. For the irradiation experiments, the solution was irradiated with cobalt-60 gamma rays for 25 min. (about 14000 r by the Fricke dosimeter) at the middle stage of the heating procedure, kept at a given temperature. (Cf. Part I). The reference experiment without the middle stage was also made as in Part I. The heating procedure is shown schematically Fig. 1.

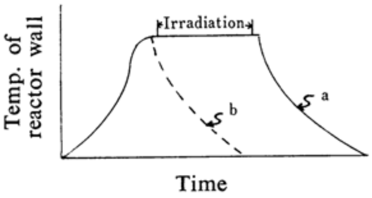

Fig. 1. Schematic heating procedure.
a) Actual experiment
b) Reference experiment

Analytical.—The produced phenol was first extracted from 1 ml. of the aqueous phase as an ether solution after the addition of 2 N hydrochloric acid. After the separation of acidic products from the ether solution by agitating with 5% sodium bicarbonate, phenol was again extracted in 1 N sodium hydroxide, and then, after being acidified by 2 N hydrochloric acid, extracted in ether. The phenol, in the benzene phase and mixed with iron precipites, was extracted together in 2 N sodium hydroxide, and then treated by the above procedure.

The amount of phenol in the above extract was determined from the optical density at 273.5 mμ ($\varepsilon=2167$), because Goodman and Steigman recommended the separation by ether[8]. The absorption curve of the extract was identical with that of pure phenol. In all cases, no biphenyl was found in the ether extract by gas-chromatography through a polyethylene-glycol column at 180°C.

The analytical methods for iron species were the same as in Part I.

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Preliminary Experiment.—When the reactants were put directly in the reactor using no glass tube, reaction seemed to be promoted considerably above 150°C with corrosion of the stainless-steel wall. Next, the reaction was carried out in a Teflon tube set tightly in the reactor in order to prevent the corrosion effect. The yield of phenol was less in a Teflon tube than in a glass tube. The yield seemed to be the highest for 0.01M salt solutions. The present experimental conditions were decided on the basis of these results.

Results

Phenol Yield in Ferric Solutions.—The total yields of phenol produced in the ferric sulfate solution of 0, 0.01 and 0.1 N sulfuric acid (0.01M of ferric ion) are shown in mg. in Fig. 2 for the cases of irradiation (solid marks and solid lines) and non-irradiation (open marks and dotted lines), and, further, by crosses for the non-irradiated 1.0 N sulfuric acid solution. No phenol was found in any of the reference experiments. In general, as the acidity increases, the maximum yield at higher temperatures decreases, and the difference between the irradiated and non-irradiated systems disappears.

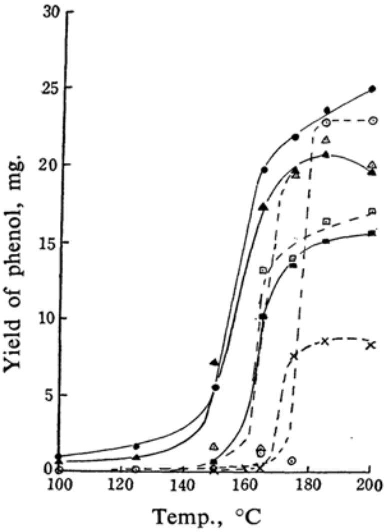


Fig. 2. Yield of phenol in 0.01M-Fe ferric sulfate solutions with radiation (solid marks) and without radiation (open marks) in neutral (● and ⊙), in 0.01N (▲ and △), in 0.1N sulfuric acid (■ and ▣), and in 1.0 N sulfuric acid without radiation (×).

The results for 0.01M ferric chloride solutions in hydrochloric acid are shown in Fig. 3 in the same manner. The tendency of the yield is almost the same, but the yield is considerably suppressed by chloride ions.

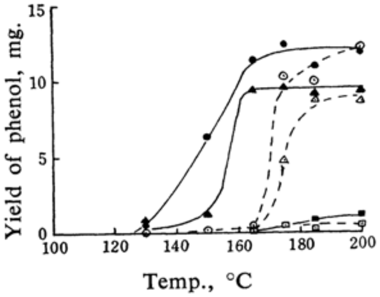


Fig. 3. Yield of phenol in 0.01M ferric chloride solutions with radiation (solid marks) and without radiation (open marks) in neutral (● and ⊙), in 0.01N (▲ and △) and 0.1N hydrochloric acid (■ and ▣).

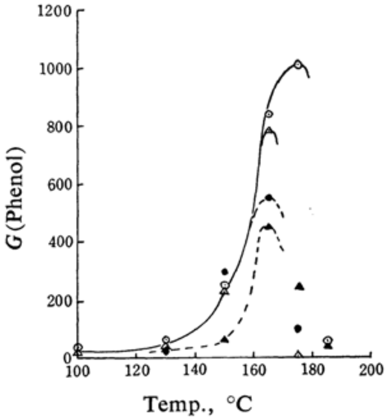


Fig. 4. G(Phenol) in ferric sulfate solutions (open marks) and in ferric chloride solutions (solid marks) ; in neutral (⊙ and ●) and in 0.01N acid (△ and ▲). G-values are evaluated as mentioned in text.

The contribution of radiation is shown in Fig. 4 by the G-value of phenol, estimated as the number of phenol molecules per 100 eV. of energy absorbed in 15 g. water, from the difference between the values of irradiated and non-irradiated systems plotted in Figs. 2 and 3.

Iron Concentration in Ferric Solutions after Reaction.—The total iron concentrations dissolved in the solutions of ferric sulfate and chloride after experiment, determined by the oxine method, are shown in Figs. 5 and 6 (the same marks as Figs. 2 and 3). The result for the ferric chloride solution in 0.01 N hydrochloric acid was almost the same as for that in the neutral solution. The precipitation reaction of iron salts seems to be somewhat retarded by phenol production as has been pointed out in Part I[4].

The ferrous content of these total iron species in the solutions, determined by the α, α'-dipyridyl method, is shown in Fig. 7 for the non-irradiated ferric sulfate solutions and in Fig. 8 for the irradiated ones, using the same marks as in Fig. 2; and in Fig. 9 for the non-irradiated and irradiated ferric chloride solutions, using the same marks as in Fig. 3.

The ferrous concentration in these figures has a maximum, and increases with increase of

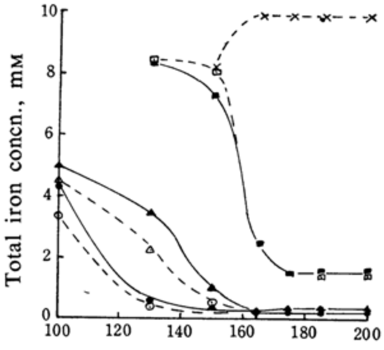


Fig. 5. Total iron concentration in ferric sulfate solutions after experiment shown in Fig. 2; marks are the same with Fig. 2.

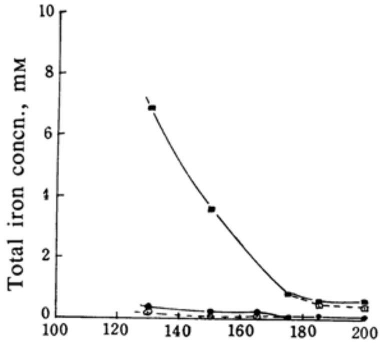


Fig. 6. Total iron concentration in ferric chloride solutions after experiment shown in Fig. 3; marks are the same with Fig. 3.

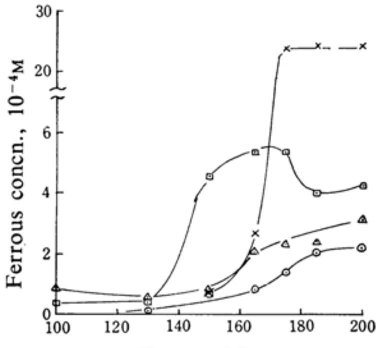


Fig. 7. Ferrous content in total iron concentrations shown in Fig. 5, for non-irradiated ferric sulfate systems; marks are the same with Fig. 2.

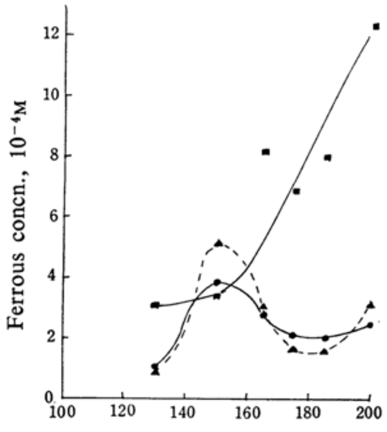


Fig. 8. Ferrous content in total iron concentrations shown in Fig. 5 for irradiated ferric sulfate systems; marks are the same with Fig. 2.

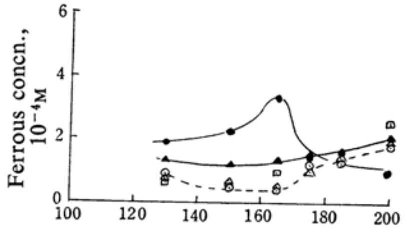


Fig. 9. Ferrous content in total iron concentrations shown in Fig. 6 for ferric chloride systems; marks are the same with Fig. 3.

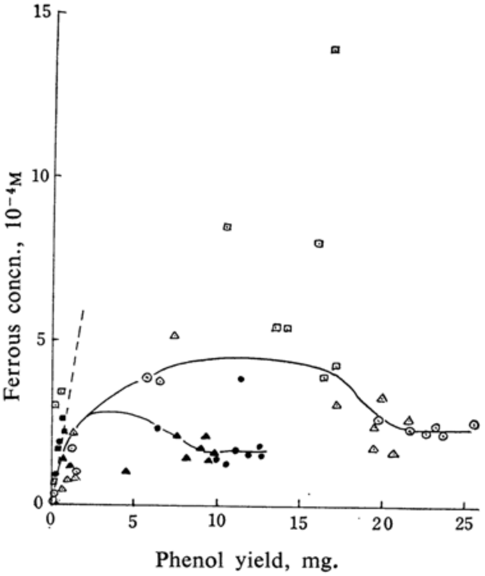


Fig. 10. Relationship between phenol yield and ferrous ion produced in ferric sulfate (open marks) and ferric chloride (solid marks) solutions in neutral (⊙ and ●), 0.01N (△ and ▲) and 0.1N (▣ and ■) acids.

acidity. Moreover, the ferrous proportion of iron species increases as the reaction temperature rises. The iron species is mostly ferrous above 180°C. Such reduction in ferric ions is never found for ferric solutions without benzene, as has been mentioned in the ferric results of Part I[4]. When all the ferrous concentrations observed are plotted against the corresponding phenol yields as in Fig. 10, there is the interesting relationship. The decrease in the ferrous concentration at the high phenol yield is due to thermal precipitation at higher temperatures[4]. In fact, the hardly precipitated systems give the high ferrous yield instead of such a decrease.

Phenol Yield in Ferrous Solutions.—The yields of phenol in 0.01M ferrous sulfate solutions are shown in Fig. 11 using the same marks as in Fig. 2. Since the yield seems to increase with the lapse of time after the preparation of the solution, the values are rather scattered. However, it might be concluded that the yield is larger even without radiation than in the ferric sulfate solution with radiation in Fig. 2; and that the difference between with and without radiation is minor. Even after the deduction of the yield at the reference experiment from the value shown in Fig. 11, the yield is still higher below 175°C but lower above 175°C than the irradiated ferric sulfate solution. This means that the oxidation reaction is promoted by ferrous species and apparently retarded by phenol production as will be discussed later.

The results of the ferrous chloride solution, shown in Fig. 12, indicate more clearly that the yield for the ferrous solution is independent of radiation. This yield is also suppressed by chloride ions.

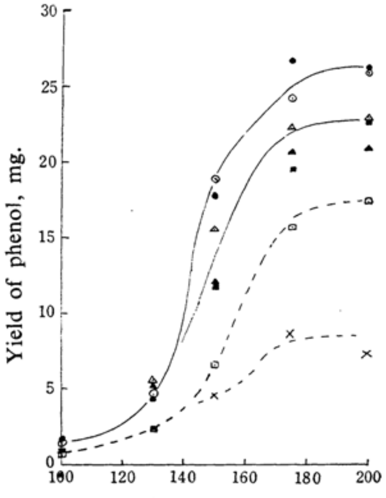


Fig. 11. Yield of phenol in 0.01M ferrous sulfate solutions; marks are the same with Fig. 2.

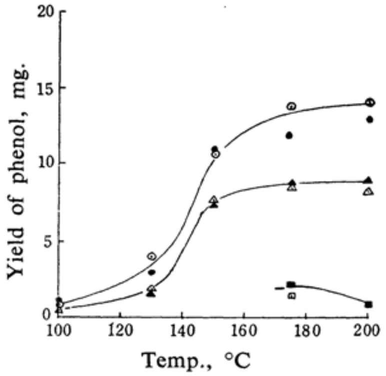


Fig. 12. Yield of phenol in 0.01 M ferrous chloride solutions; marks are the same with Fig. 3.

Iron Concentration in Ferrous Solutions after Reaction.—The concentrations of the total iron species and ferric species dissolved in the ferrous sulfate solutions after experiment are shown in Figs. 13 and 14 respectively, using

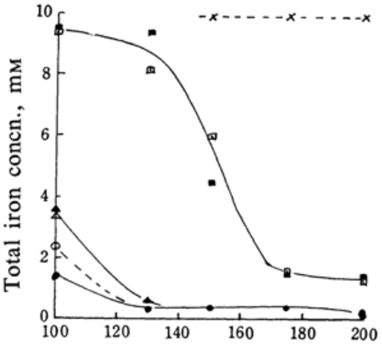


Fig. 13. Total iron concentration in ferrous sulfate solutions after experiment shown in Fig. 11; marks are the same with Fig. 2.

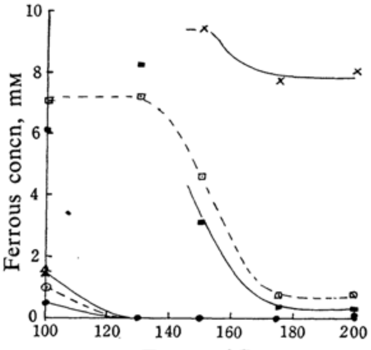


Fig. 14. Ferrous content in total iron concentrations shown in Fig. 13 for ferrous sulfate systems; marks are the same with Fig. 2.

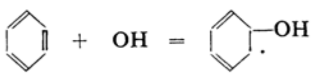
the same marks as in Fig. 2. The results are interesting in comparison with the corresponding ones without benzene in Part I[4]; there is no ferric ion above 130°C in 0 and 0.01 N sulfuric acid even though the present reactions were carried out under the high pressure of oxygen at elevated temperatures.

The results for the ferrous chloride solution were almost the same as those for the ferrous sulfate solution.

Discussion

The Effect of Radiation.—Dorfman et al. concluded, on the basis of electron-pulse radiolysis, that the radiation oxidation of benzene in an oxygenated aqueous solution at room temperature is through the following transient species[9];

$$H_2O \rightsquigarrow H,\ OH,\ H_2,\ H_2O_2 \qquad (1)$$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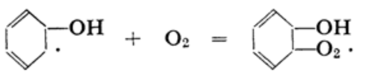
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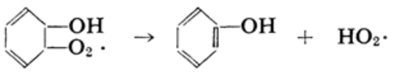

(4)

They estimated the rate of these reactions at 23°C to be $(4.3 \pm 0.9)\times 10^9 \text{M}^{-1}\text{sec}^{-1}$ for reaction 2 and $(5.0 \pm 0.6)\times 10^8 \text{M}^{-1}\text{sec}^{-1}$ for reaction 3. According to their observation, this hyroxycyclohexadienyl peroxy radical is fairly stable.

Hydrogen atom from reaction 1 combines with dissolved oxygen;

$$H + O_2 = HO_2 \qquad (5)$$

The rate of this reaction at 25°C is 1.1×10^9 $\text{M}^{-1}\text{sec}^{-1}$ in acid and $5.5\times 10^9 \text{M}^{-1}\text{sec}^{-1}$ in a neutral solution[10]. The HO_2 radical and hydrogen peroxide is converted to OH radical as discussed in the next section. Ferric ions are not reduced by products of reaction 1 when oxygen exists[11,12]. In fact, the ferrous concentration in the ferric sulfate solution without benzene does not increase upon irradiation, as has been mentioned in the results section of Part I[4].

The suppression of phenol production in the chloride solutions is due to scavenging of the initiator of reaction 2;

$$Cl^- + OH + H^+ = Cl + H_2O \qquad (6)$$

The rate of this reaction at 25°C is supposed to be $1.8\times 10^8 \text{M}^{-1}\text{sec}^{-1}$ at pH 2, and about ten times as fast as in 0.8 N sulfuric acid[13,14]. The effect of chloride ions, shown in Figs. 3 and 12, can be understood qualitatively by comparing these rates with the rates of reaction 2 and of reaction 11 to be discussed in the next section.

Initiation in Ferrous Solutions.—The results obtained by the same procedure in the aqueous phase containing no salt are given in Table I, in which the *G*-value in parentheses is reported by Proskurnin and Kolotyrkin[15]. Since a yield less than 0.04 mg. is unreliable, it can be said that no phenol is produced without any salt and radiation. Therefore, it is certain that the oxidation of benzene shown in Figs. 11 and 12 is neither initiated by the thermal cracking of benzene nor by the hydrogen abstraction of oxygen from benzene.

TABLE I. PHENOL YIELD WITHOUT IRON SALTS

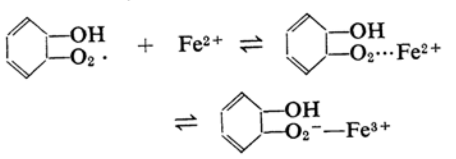
Medium	Radiation	Yield mg.	Yield *G*-Value
Water	Yes	0.33	16, (20)[15]
	No	0.02	—
0.1 N H_2SO_4	Yes	0.48	24
	No	0.04	—

As has been mentioned in Part I[4], the autooxidation of ferrous ions in an aqueous solution has usually been interpreted by the reaction

$$Fe^{2+} + O_2 + H^+ = Fe^{3+} + HO_2 \qquad (7)$$

Even if the HO_2 radical can not react directly with benzene, it can be converted to OH radical in the presence of ferrous ions. Therefore, it can be assumed that the oxidation of benzene in the ferrous solution is initiated by OH radical produced through reaction 7 and proceeds like reactions 2 and 3 even without reaction 1.

When the oxidation process is initiated through these reactions, hydroxycyclohexadienyl peroxy radical of reaction 3 is considered to be complexed in the ferrous solution in this manner;


(8)

as is usually assumed for the catalytic action

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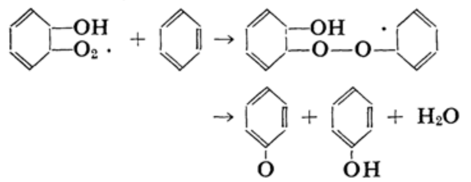
of redox ions[16]. Since such complexing stabilizes further the peroxy radical which has a fairly long life as has been pointed out already[9], the peroxy radical is allowed to react with benzene in this manner[17];


(9)

(10)

as well as via reaction 4. However, reaction 9 seems to have a threshold temperature.

The rate of reaction 7 at 150°C is 6×10^{-4} sec^{-1} in 0.1 N sulfuric acid under the present experimental conditions as was estimated in Part I[4]. Although OH radical is scavenged by ferrous ions thus;

$$\mathrm{Fe^{2+} + OH = Fe^{3+} + OH^-} \qquad (11)$$

where the rate of this reaction is $2.6\times10^{8}\,\mathrm{M^{-1}\,sec^{-1}}$ at pH 2 and 25°C[13], the rate of reaction 2 is very fast as has been mentioned already. According to the earlier results[14], the rate of reaction 2 at 25°C is 3.2 times as fast as that of reaction 11.

It may be open to doubt about the stability of the HO_2 radical and of hydrogen peroxide at elevated temperatures, especially in the presence of ferrous ions. The rate of the decomposition reaction

$$\mathrm{Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + OH} \qquad (12)$$

is supposed to be $6.6\times10^{3}\,\mathrm{M^{-1}sec^{-1}}$ at 150°C from extrapolation of the finding of Barb et al.[18], who extensively studied this subject in the room temperature range. The rate of reaction 2 is further faster than this rate. In any case, the present fact of phenol production is a good answer to the doubt.

When Figs. 2 and 11 are compared with Figs. 3 and 12, the yield of phenol in the non-irradiated ferrous solutions is almost the same as that in the irradiated ones, and it is larger than in the irradiated ferric solutions. Therefore, the overall yield of OH radicals by these thermal reactions seems to be considerably higher in spite of reacction 11, than by radiation-induced reaction 1 and reaction 5.

Initiation in Ferric Solutions.—Among the primary products of reaction 1, in the irradiated ferric solution, the OH radicals are not only scavenged like reaction 11, but they can also not be converted from the hydrogen atom and hydrogen peroxide, through reactions 5 and 12, to initiate the oxidation process. Therefore, the high yield of phenol is supposed also to be due to the complexing of the peroxide radical from reaction 3, with a trace amount of ferrous ions being present initially, as has been pointed out in Part I[4].

On the other hand, the oxidation process is also initiated without radiation in the ferric solution above 170°C, as is shown in Fig. 2. It can be understood similarly if ferrous ions are produced by any reaction in the ferric solution. Some reports seem to suggest such a possibility[19-21]. Recently the reaction

$$\mathrm{2Ce^{4+} + H_2O \rightarrow 2Ce^{3+} + \frac{1}{2}O_2} \qquad (13)$$

was assumed to account for the fact that cerric ions are reduced thermally in sulfuric acid at elevated temperatures[22]. Dobson and Hughes also discussed the possibility of ferric reduction in an irradiated ferric aqueous solution[12]. As if suggesting a process like reaction 13, the ferric solution gave an trace amount of ferrous species by about $2\times10^{-5}\,\mathrm{M}$ as pointed out above.

Propagation Processes.—After reaction 10, the oxidation process of benzene is propagated through the following reactions [6,7,23]:

$$\mathrm{PhO + PhH = PhOH + Ph} \qquad (14)$$

$$\mathrm{Ph + O_2 = PhO_2} \qquad (15)$$

$$\mathrm{PhO_2 + PhH = PhO_2H + Ph} \qquad (16)$$

$$\mathrm{PhO_2H + Fe^{3+} = PhO_2 + H^+ + Fe^{2+}} \qquad (17)$$

$$\mathrm{PhO_2H + Fe^{2+} = PhO + OH^- + Fe^{3+}} \qquad (18)$$

(Ph: Phenyl radical)

in the iron solution, since ferrous and ferric ions are present together at once even if the reaction starts either with the pure ferrous or ferric solution.

Ferric ions are reduced considerably with phenol production as has been mentioned in the description of Fig. 10. This fact cannot be interpreted without the aid of reactions 10, 14 and 17. In the interpretation of Fig. 10, it should be noticed that some of the ferrous ions produced by reaction 17 are reoxidized by other reactions and precipitated, as has been mentioned already. Among the related reactions, the rate of the precipitation reaction in the neutral ferric sulfate solution is

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$2.5\text{M}^{-1}\text{sec}^{-1}$ at 150°C, as has been estimated in Part I[4]. The rate of the oxidation reaction 7 is slow as mentioned already. Although no report has been found on the decmposition of phenyl hydroperoxide, the rate of cumene hydroperoxide decomposition, as in reaction 17 in the presence of oxygen, is supposed to be $1.6\times10^4\text{M}^{-1}\text{sec}^{-1}$ at 150°C by extrapolation from the equation of Fordham and Williams[24]. Therefore, the rate of phenyl hydroperoxide decomposition is supposed to be the same order or faster than this rate, due to the high resonance energy of phenoxy radical[25,26]. At any rate, ferrous ions accumulate first with phenol production, as the reaction temperature rises, but the concentration decreases due to the precipitation at higher temperatures.

The mole ratio of the amount of ferrous ions to phenol is 0.46 ± 0.02, judging from the results at 175, 185 and 200°C in the non-irradiated 1.0 N sulfuric acid solution, which gave scarcely any precipitate. This ratio is represented by the dotted line in Fig. 10. Since ferrous ions for reaction 18 are produced only by reaction 17 in the ferric solution, this ratio means that the contribution of reaction 17 is greater than reaction 18, but not necessarily that the rate of the former is faster than that of the latter, when taking account of the difference between the initial concentrations of ferrous and ferric ions. In general, the dissociation energy of the O–O bond in hydroperoxide is smaller than the O–H bond. Especially, the decomposition

$$\text{PhOOH} = \text{PhO} + \text{OH} \tag{19}$$

should be fast, even without redox ions, as has been discussed above[25].

Termination and Retardation Processes.—The yield of phenol hardly increases with rise of temperature at higher temperatures as at lower temperatures. Such saturation of the phenol yield is mainly attributed to the oxidation decomposition of phenol produced[27] rather than to the self-inhibition effect of phenols on oxidation reactions[28].

The other by-reactions between the reactants of the above reactions are also minor as the termination and retardation processes. For example, the present oxidation process is not terminated, as would usually be expected, by the reaction between phenyl peroxide;

$$2\text{PhO}_2 = \text{PhO–OPh} + \text{O}_2 \tag{20}$$

as biphenoxy should be decomposed at least at elevated temperatures thus;

$$\text{PhO–OPh} = 2\text{PhO} \tag{21}$$

due to the repulsion between the high dipoles[7]; that is, the overall reaction can be expressed as

$$2\text{PhO}_2 = 2\text{PhO} + \text{O}_2 \tag{22}$$

Such a reaction is confirmed for cumene peroxide[6]. However, reaction 20 might play part in the retardation process at higher temperatures, at which phenyl peroxide is concentrated.

Effect of Acid Concentration.—As the acidity increases, the yield of phenol decreases due to the decrease of the concentration for the effective reactants of reactions 8 and 18. The reactivity of ions is very sensitive to the state in a solution, either free or complexed, dependent on the acidity[11].

The other effect of acids is as an anion, as in reaction 11. The decomposed products of sulfate ions might initiate the oxidation process of benzene in the concentrated acid solution.

Summary

In the ferric sulfate solution, benzene can be oxidized to phenol with a good yield above 170°C, when not irradiated, but at lower temperatures, when irradiated. In the ferrous sulfate solution, the yield of phenol is independent of irradiation, and somewhat larger than in the irradiated ferric sulfate solution. Such a high yield of phenol is due to the complexing of hydroxycyclohexadienyl peroxy radical, produced with OH radical and oxygen dissolved, with ferrous ions.

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