Thermal and Radiation Oxidations of Benzene to Phenol in Aqueous Solutions Containing Metal Ions at Elevated Temperatures. III.[1,2]

The Effect of Copper Ions

By Hiroshi HOTTA, Nobutake SUZUKI and Akira TERAKAWA[3]

(Received April 18, 1963)

In this paper the results of the oxidation of benzene to phenol in cupric aqueous solutions will be discussed and will be compared with the results for iron salt solutions reported in Part II.[2] The most distinctive point is that cuprous ions are unstable because of the fast rate of oxidation by the oxygen dissolved in contrast to ferrous ions which are stable.

Experimental

Aqueous Solutions.—Cupric sulfate was dissolved initially by 0.01 M in 0, 0.01 and 0.1 N sulfuric acid; cupric chloride was similarly dissolved in hydrochloric acid. All reagents were of guaranteed grade.

Apparatus and Procedure. — The experimental procedure, described in detail previously,[1,2] may be outlined as follows: 1 cc. of benzene was put on 15 cc. of an aqueous solution in a hard-glass tube set in a 50 cc. stainless-steel reactor under an oxygen pressure of 30 atm., and then this system was heated by the programming heater and kept for 30 min. at a given temperature. When irradiated by cobalt-60 gamma rays, the dose was about 14000 r. for 25 min.

Analytical.—The yield of phenol was determined from the optical density of the ether extract at 273.5 mμ, as in Part II.[2]

The concentration of cupric species dissolved in the solution after reaction was determined from the optical density of the cupric-oxine complex in chloroform.[4] The concentration of ferrous species was measured in the form of the α, α'-dipyridyl complex.

Results and Discussion

The Irradiated Solutions of Cupric Sulfate.—The total amount of phenol produced in the irradiated 0.01 M cupric sulfate solutions of 0, 0.01 and 0.1 N sulfuric acid is plotted as the function of the reaction temperature by the solid marks and the solid lines in Fig. 1. A small amount of precipitates was found only at temperatures higher than 180°C, in contrast to the case of iron salts.[1]

---

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

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

[3] Present address: Showa Denko Co., Minato-ku, Tokyo.

[4] K. Motojima and H. Hashitani, *Japan Analyts* (*Bunseki Kagaku*), **9**, 151 (1960).

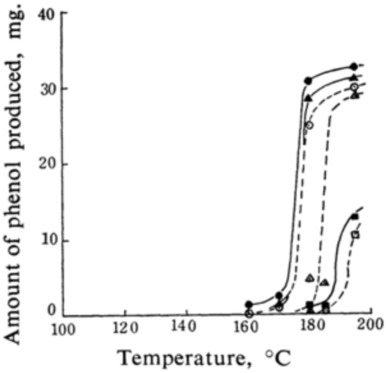
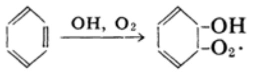


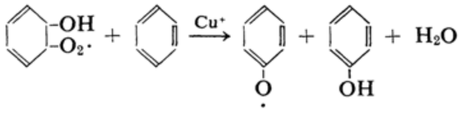
Fig. 1. Yields of phenol in 0.01 M cupric sulfate solutions with radiation (solid marks) and without radiation (open marks) in neutral (● and ⊙), in 0.01 N (▲ and △) and in 0.1 N (■ and ▣) sulfuric acid.

According to Part II,[2] the reaction scheme of the radiation oxidation of benzene in an aerated aqueous solution of copper salt at elevated temperatures is assumed to be as follows:

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



(2)



(3)

$$PhO + PhH = PhOH + Ph \qquad (4)$$

$$Ph + O_2 = PhO_2 \qquad (5)$$

$$PhO_2 + PhH = PhO_2H + Ph \qquad (6)$$

$$PhO_2H + Cu^{2+} = PhO_2 + H^+ + Cu^+ \qquad (7)$$

$$PhO_2H + Cu^+ = PhO + OH^- + Cu^{2+} \qquad (8)$$

(Ph: phenyl radical)

In ferric sulfate solutions, it was assumed in Part II that the initiation of the chain oxidation of benzene (reaction 3) is to be attributed to a trace amount of ferrous ion present initially, as ferric ions are reduced successively through the propagation process (cf. reaction 7) once initiated. However, in cupric sulfate solutions, such a cuprous ion propagating the chain process (reactions 3 and 8) cannot be present, for cuprous ions, unlike ferrous ions, are readily oxidized by oxygen. Therefore, scarcely any phenol is produced up to 160°C, as Fig. 1 shows, unlike the case of ferric sulfate solutions.[2]

Phenol production is considerably suppressed in the 0.1 N sulfuric acid. This is mainly due to the acceleration of cuprous oxidation;

$$Cu^+ + O_2 + H^+ = Cu^{2+} + HO_2 \qquad (9)$$

On the other hand, as the open marks and dotted lines in Fig. 1 show, phenol is produced in the non-irradiated solutions at somewhat higher tempetatures than in the irradiated ones.

The Effect of Copper Metal in the Sulfate Solutions.—The amounts of phenol produced in the solutions with the composition given in Table I and containing 2 g. of copper metal pieces (99.99% purity), are shown in Fig. 2 by solid marks for the irradiated cases and by open marks for the non-irradiated cases. As Fig. 2 shows, when copper metal is present in the aqueous phase, the yield of phenol is large, even at lower temperatures, regardless of irradiation or non-irradiation, as in the ferrous solution.[2] This is especially clear in solution a.

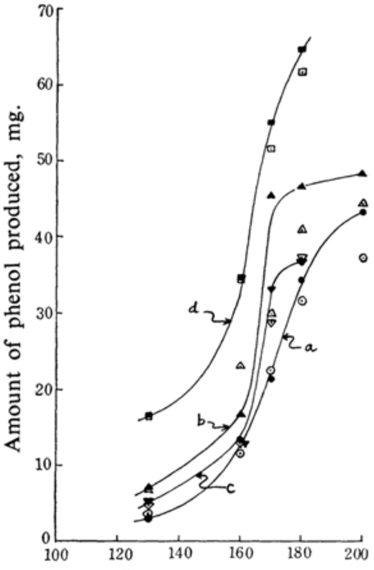


Fig. 2. Yields of phenol in (a) neutral 0.01 M cupric sulfate solution (● and ⊙), (b) 0.01 M cupric sulfate solution of 0.01 N sulfuric acid (▲ and △), (c) 0.01 N sulfuric acid (▼ and ▽) and (d) 0.1 N sulfuric acid (■ and ▣) with radiation (solid marks) and without radiation (open marks). These systems contained 2 g. of copper metal pieces, respectively.

This fact supports the above assumption that scarcely any production of phenol in the cupric solution below 160°C is due to the lack of cuprous ions. Since cuprous ions are supplied continuously by the corrosion of the copper metal, the yield of phenol increases with an increase in the acidity. The concentration of cupric species in the solution after the reaction, given in Table I, is almost the same over the entire temperature range,

TABLE I. EFFICIENCIES OF COPPER METAL DISSOLVED FOR PHENOL PRODUCTION

System	Composition			Temp.	γ-Rays	Phenol produced to metal dissolved,	(Cu^{2+}) after reaction
	H_2SO_4 N	$CuSO_4$ M	Cu-metal g.	°C		mole ratio	M
a	0	0.01	2	160	Yes	>300	0.0101
					No	130	0.0107
				170	Yes	110	0.0114
					No	260	0.0106
b	0.01	0.01	2	160	Yes	27	0.0143
					No	20	0.0182
				170	Yes	83	0.0139
					No	24	0.0188
c	0.01	0	2	160	Yes	12	0.0078
					No	12	0.0079
				170	Yes	23	0.0089
					No	27	0.0087
d	0.1	0	2	160	Yes	5.5	0.0447
					No	5.4	0.0448
				170	Yes	8.4	0.0465
					No	8.5	0.0434

independent of the increase in phenol yield. As the acidity increases, the number of metal ions dissolved increases, as does the yield of phenol. Therefore, the efficiency of the copper metal dissolved for phenol production, i. e., the mole ratio of the phenol produced to the copper metal dissolved, is the greatest for the neutral solution a, as Table I shows. This means that the majority of the cuprous ions produced from metal are oxidized by oxygen independent of the phenol production.

It should be noticed that phenol production is accelerated even for the case of solution a in Fig. 2, in which the concentration of cupric species increases only a little. This means that a trace amount of cuprous ions is sufficient to initiate the chain process. When a solution containing cupric ions is in contact with copper metal, the equilibrium constant of the disproportionation,

$$Cu^{2+} + Cu \rightleftharpoons 2Cu^{+} \qquad (10)$$

is

$$K_{10}=\frac{\sqrt{(Cu^{2+})}}{(Cu^{+})}=10^{3}$$

at room temperature.[5] The production of cuprous ions in the neutral solution may be due to a slight corrosion of copper metal by the decomposed product of sulfate ions as well as to reaction 10.

It may be concluded from the mole ratios in Table I that the chain length of the oxidation reaction is at least 100 for 10 mg. of phenol produced. On the other hand, the *G*-value of phenol is 320 for 10 mg. of phenol produced at 160°C in the irradiated neutral ferric sulfate solution (from Figs. 2 and 4 in Part II.[2] For this case, it is supposed that the apparent *G*-value of OH radical as the initiator of phenol production (reaction 2) is less than 3 in spite of the various paths for the OH radical production (cf. Part II), if one assumes that the efficiencies of ferrous and cuprous ions are equivalent for the whole chain process.

Cupric-Ferric Solutions. — In the aerated cupric-ferric solution at room temperature, ferrous ions are produced due to the reactions[6-8]

$$Cu^{2+} + HO_2 = Cu^{+} + H^{+} + O_2 \qquad (11)$$

and

$$Cu^{+} + Fe^{3+} = Cu^{2+} + Fe^{2+} \qquad (12)$$

However, in the cupric solution without ferric ions under high oxygen pressure at elevated temperatures, since cuprous ions are not scavenged by ferric ions if reduced, the equilibrium between reactions 9 and 11 depends on the oxygen pressure. Therefore, cupric ions are considered not to be reduced by reaction 11 in the solutions in Fig. 1.

Moreover, even in the irradiated and non-irradiated neutral and 0.1 N sulfuric acid solutions of 0.01 M cupric-0.01 M ferric[9] sulfate,

---

[5] I. Grenthe, *J. Am. Chem. Soc.*, **83**, 360 (1961).

[6] E. J. Hart, *Radiation Research*, **2**, 33 (1955).

[7] W. G. Barb, J. H. Baxendale, P. George and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462 (1951).

[8] M. Cher and N. Davidson, *J. Am. Chem. Soc.*, **77**, 793 (1955).

[9] The concentration of 0.01M is not of ferric sulfate but of ferric ions.

in fact, ferrous ions were not produced, indicating that cupric ions are seemingly not reduced after all.

Next, benzene was oxidized in this neutral cupric-ferric solution. The amount of phenol produced (triangle marks) and the ferrous concentration (circle marks) are shown in Fig. 3 by solid marks for the irradiated case and by opon marks for the non-irradiated case. The ferrous concentration less than 1×10^{-5} M is unreliable.

In Fig. 3, the yield of phenol is much smaller than in the respective 0.01 M cupric and 0.01 M[9] ferric sulfate solutions, and scarcely any phenol is produced, even at 190°C, in the non-irradiated cupric-ferric solution. This means that, even if ferrous ions are produced by the oxidation process of benzene, they are reoxidized by the back path of reaction 12, and then the cuprous ions produced are consumed at once by the excess oxygen. Therefore, the oxidation process of benzene cannot be propagated successively. The mole ratios of the phenol produced to the ferrous concentration for the irradiated case are 22 and 54 at 170°C and 190°C respectively (cf. Fig. 3), suggesting such a consumption of ferrous ions.

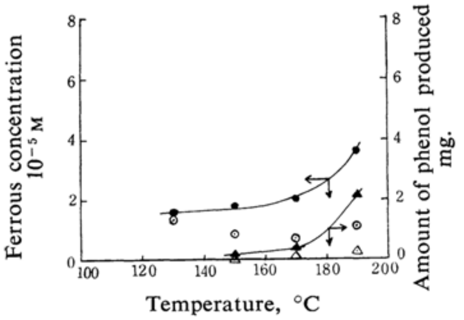


Fig. 3. Yields of phenol in the irradiated (▲) and non-irradiated (△) 0.01 M cupric-0.01 M ferric sulfate solution, and the corresponding ferrous concentrations (● and ⊙) after reaction.

These ratios are much larger than in the iron salt solutions discussed in Part II.[2] That is, the fast rate of cuprous oxidation kills not only the activity of cuprous ions but also that of ferrous ions.

Cupric Chloride Solutions.—The results of cupric chloride solutions in 0, 0.01 and 0.1 N hydrochloric acid are shown in Fig. 4 by marks similar to those in Fig. 1. Phenol production is suppressed in the presence of chloride ions, as has been seen in the iron chloride solution.[2]

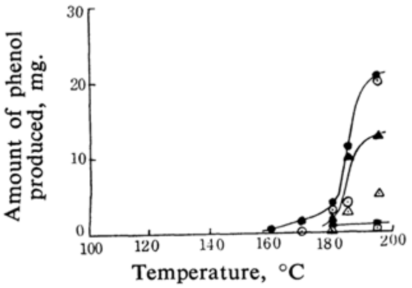


Fig. 4. Yields of phenol in 0.01 M cupric chloride solutions with radiation (solid marks) and without radiation (open marks) in neutral (● and ⊙), in 0.01 N (▲ and △) and in 0.1 N (■ and ▣) hydrochloric acid.

Summary

The yield of phenol increases abruptly above 170°C in the cupric sulfate solutions. When the solutions contain copper metal pieces, phenol is produced, even below 160°C, regardless of irradiation or non-irradiation. On the other hand, scarcely any phenol is produced in the cupric-ferric sulfate solution, even at 180°C. These facts are to be attributed to the fast rate of cuprous oxidation by oxygen.

Japan Atomic Energy Research Institute
Tokai, Ibaraki-ken