Effect of Cupric Ion on Oxidation of Benzene Aqueous Solution by Cobalt-60 Gamma-rays

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The oxidation of benzene aqueous solution by Cobalt-60 gamma-rays has been studied by some investigators[1-4]. The yields of phenol and biphenyl are affected by the presence of some metallic ions[5-7]. The effect of cupric ions will be interpreted in the present paper.

Experimental

Triply distilled water was saturated with benzene purified by sulfuric acid and then by freezing, by shaking in a separate funnel. Then some solutions were aerated in a gas-wash bottle on covering the solution with benzene. Other inorganic reagents were used without further purification. The concentrations of initial benzene and produced phenol were measured directly by optical density at 253.5 and 270 mμ, respectively.

The solution in a test tube of hard glass (Hario Glass) was irradiated at the Cobalt-60 Irradiation Laboratory of Japan Atomic Energy Research Institute at room temperature (ca. 20°C). The dose, which was measured chemically as mentioned elsewhere[8], was changed not by its irradiation time, but by irradiation for one hour at various positions, namely, at various dose rates. Therefore, the abscissa of Fig. 1 gives the value of the dose in r as well as the value of dose rate in r/hr.

Results

The results of aerated benzene-saturated aqueous solution containing (a) 0.8 N sulfuric acid or (b) nothing are shown in Fig. 1. These curves were linear up to ca. $4\times10^4\,r$ for both solutions. The white precipitate, which smelled like biphenyl, was found in the solution irradiated by more than $7\times10^4\,r$, and was separated by means of a centrifuge for the measurement of optical density. The corresponding G-value of phenol is listed in Table I with the composition of each solution.

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[1] P. V. Phung and M. Burton, *Radiation Research*, **7**, 199 (1957).

[2] K. C. Kurien, P. V. Phung and M. Burton, ibid., in press.

[3] G. Stein and J. Weiss, *J. Chem. Soc.*, **1949**, 3241.

[4] M. A. Proskyrnin, *Atomnaya Energiya* (*USSR*), **5**, 321 (1958).

[5] M. A. Proskyrnin and E. V. Barelko, *Nuclear Sci. Abstr.*, **13**, 1020 (1959).

[6] J. H. Baxendale and D. Smithies, *J. Chem. Soc.*, **1959**, 779.

[7] T. Yumoto, Y. Bono and T. Matsuda, *Mem. Gov. Ind. Research Inst. Nagoya* (in Japanese), **8**, 296 (1959).

[8] H. Hotta, A. Terakawa and S. Ōno, to be published.

TABLE I. YIELD OF PHENOL

Name	Solute (in M)				Treatment	G-value	
	Cupric sulfate	Cupric chloride	Sulfuric acid	Benzene		At low dose	At high dose
a	0	0	0.4	Saturated	Aerated	2.63	0.33
b	0	0	0	Saturated	Aerated	2.63	(0.64)*
c	0.01	0	0.4	0.0115	Not-aerated	5.98±1.1	0.68±0.03
d	0	0.01	0.4	0.0132	Not-aerated	3.63±0.9	0.55±0.14
Burton[1]	0	0	0.4	Saturated	—	(2.64±0.04)**	(0.35±0.02)***

* Less reliable; ** Aerated; *** Oxygen-free.

The G-value of solution b) at a high dose was less reliable.

The results of benzene-saturated 0.8 N sulfuric acid solutions containing (c) 0.01 M cupric sulfate or (d) 0.01 M cupric chloride, which were not aerated, are also shown in Fig. 1. These curves were linear up to ca. $6\times10^4\,r$ for both solutions. These solutions smelled somewhat like biphenyl at a higher does than that corresponding to the break point of the curve. However, nothing was found as precipitate even at the highest dose in spite of the presence of a break point. The corresponding G-value is greater than that in the absence of any cupric ion as listed in Table I.

The earlier result by Burton et al. is listed in the same table for reference[1].

According to the examination of the analytical method by Goodman and Steigman[9], the spectroscopic method without solvent extraction as employed in the present work unavoidably gives a higher G-value of phenol (ca. 29% higher). However, the following discussion might not be proved valueless qualitatively by this uncertainty. Kurien, Phung and Burton indicate that their initial G-value of phenol is very correctly 2.64[2], which is nearly equal to the present value.

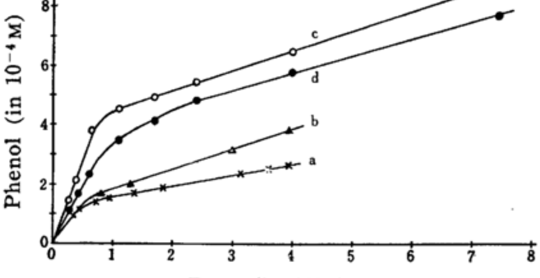

Fig. 1. Oxidation of aqueous benzene solutions. The name of each curve corresponds to the condition in Table. 1.

Discussion

According to Burton et al.[1,2], phenol and hydrogen peroxide are produced by irradiation of aerated aqueous solution saturated with benzene like the present solutions a) and b). They interpret this fact with the following reactions:

$$H_2O \rightsquigarrow H,\ OH,\ H_2,\ H_2O_2 \quad (0)$$

$$PhH+OH=Ph+H_2O \quad (1)$$

$$Ph+O_2=PhO_2 \quad (2)$$

$$PhO_2+H_2O=PhOH+HO_2 \quad (3)$$

$$H+O_2=HO_2 \quad (4)$$

and

$$2HO_2=H_2O_2+O_2 \quad (5)$$

Furthermore, the reactions,

$$Ph+OH=PhOH \quad (6)$$

$$Ph+Ph=Ph_2 \quad (7)$$

$$PhH+H=PhH_2 \longrightarrow \text{Polymer} \quad (8)$$

and

$$Ph+H=PhH \quad (9)$$

must be considered in the oxygen-free or -nearly free solution. Reactions 7 and 8 give some insoluble products. According to Baxendale and Magee[10], the reaction

$$Ph+H_2O_2=PhOH+OH \quad (10)$$

does not occur. Ph in the above equations denotes phenyl radical (C_6H_5).

The above interpretation is based on the assumption that, since the oxygen molecule scavenges all of the phenyl radical as well as H atoms, reactions 7 and 8 are suppressed by oxygen. The yield of phenyl depends not on the concentration of benzene but on that of oxygen. The concentrations at the break point of the curve are supposed to be about 1×10^{-2} M and 1×10^{-4} M for benzene and oxygen, respectively, from the former

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[9] J. Goodman and J. Steigman, *J. Phys. Chem.*, **62**, 1020 (1958).

[10] J. H. Baxendale and J. Magee, *Discussions Faraday Soc.*, **14**, 160 (1953).

and the present experiments[1,11]. In a concentration of oxygen lower than this, phenol radicals are consumed by reactions 6—9[1,6]. The yield of phenol by the above reactions is at the highest $G_w(OH)=2.92$, which is the G-value of the OH radical induced from water. In fact, the experimental G-value supports this restriction, and indicates the partial re-hydrogenation of the phenyl radical to benzene by reaction 9, since the value is smaller than $G_w(OH)$.

In the presence of a cupric ion, the yield of phenol is larger than $G_w(OH)$, and no insoluble product is yielded even at the highest dose. The large yield of phenol can be interpreted by the following reactions,

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

and then

$$Cu^{+}+H_2O_2=Cu^{2+}+OH^{-}+OH \qquad (12)$$

The highest yield of phenol from this interpretation is $G_w(OH)+G(H_2O_2)=2.92+2.84=5.76$, where $G(H_2O_2)$ denotes the G-value of hydrogen peroxide by reaction 5 as well as reaction 0 and is estimated from datum by Phung and Burton[1]. Of course, a part of OH radicals may be consumed by the reaction

$$Cu^{+}+OH=Cu^{2+}+OH^{-} \qquad (13)$$

This highest G-value is nearly equal to the present observed value of solution c) in Table I. The rate constant of reaction 11 is quantitatively confirmed to be great in the experiment of aqueous ferrous-cupric solution[8].

The concentration of benzene is not necessarily slight at the break point, and benzene should scavenge almost all of the OH radical by reaction 1 even after the break point as well as in the initial stage. Therefore, since the yield of phenyl radical is independent of oxygen, the fate of phenyl radicals, which are not dimerized to biphenyl by reaction 7 in virtue of the presence of the cupric ion, must be considered beside reaction 9. Moreover, reaction 11 suppresses reaction 9. Although reaction 11 suppresses also reaction 8, it is independent of phenyl radical. When the negative phenyl ion, Ph^-, is assumed to be a more stable form than phenyl radical, the promotion of re-hydrogenation to benzene without dimerization due to the cupric ion can be interpreted by the reactions,

$$Ph+Cu^{+}=Ph^{-}+Cu^{2+} \qquad (14)$$

and then $$Ph^{-}+H^{+}=PhH \qquad (15)$$

through reaction 11. An analogous reaction is assumed for ferrous ion by Baxendale and Magee[10]. If almost all of the radical induced from water is scavenged by reactions 1 and 11 in the present condition, reactions 14 and 15 enable them to understand why no precipitate is found even at the highest dose in the presence of a cupric ion. The decomposition of phenol is slight according to Kurien, Phung and Burton[2]. There was no difference for the characteristics of absorption curve between 200∼300 mμ for the solution through the whole range of dose.

Next, the effect of a chloride ion on the yield of phenol is noticed for solution d). A chloride ion is usually considered to react with OH radical in an acidic aqueous solution[12] as

$$Cl^{-}+H^{+}+OH=Cl+H_2O \qquad (16)$$

and then $$Cl+H_2O_2=Cl^{-}+H^{+}+HO_2 \qquad (17)$$

or $$Cl+H=Cl^{-}+H^{+} \qquad (18)$$

Since reaction 16 competes with reaction 1, the yield of phenol is reduced. The reaction between phenyl and chloride radicals is ignored. The detailed study of the effect of chloride ions on the radiolysis of aqueous solution will be given in a later paper[8].

Since the present experiment is not exhaustive, the detailed study will follow.

Summary

The effect of a cupric ion on the radiolysis of benzene aqueous solution can be interpreted by the following reactions of a cuprous ion produced in reaction $Cu^{2+}+H=Cu^{+}+H^{+}$. That is, the larger yield of phenol than $G_w(OH)$ in the presence of oxygen is due to the increment of OH radical by reaction $Cu^{+}+H_2O_2=Cu^{2+}+OH^{-}+OH$, and no precipitation in the absence of oxygen is due to re-hydrogenation by reactions $Ph+Cu^{+}=Ph^{-}+Cu^{2+}$ and $Ph^{-}+H^{+}=PhH$, respectively.

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[11] N. A. Lange, "Handbook of Chemistry", Handbook Publishers, Inc., Sandusky, Ohio (1956), p. 1091.

[12] T. J. Sworski, *Radiation Research*, **2**, 26 (1955).