7.61 mmol) at 0 °C over a period of 10 min. After the mixture was stirred at room temperature for 3.5 h, the resulting white precipitate was collected, washed with dry ether (20 mL), and dried over $P_4O_{10}$ to afford **31** (1.48 g, 84%): mp 104–105 °C; IR (KBr) 1705 (C═O), 1495, 1250 cm$^{-1}$. Anal. Calcd for $C_9H_{14}O_4NP$: C, 46.76; H, 6.10; N, 6.06. Found: C, 46.70; H, 7; H, 6.06; N, 5.97.

**Monoanilinium Salt of 1,2-Epoxy-1-methylethylphosphonate (32).** To a mixture of methanol (0.503 g, 15.70 mmol) and aniline (0.736 g, 7.90 mmol) in dry ether (25 mL) was added dropwise with stirring at 0 °C a mixture of **17a** (1.34 g, 4.95 mmol) and **4a** (0.46 g, 1.65 mmol), obtained in the previous experiment, in dry ether (5 mL) over a period of 10 min. After the mixture was stirred at room temperature for 3 h, the resulting white precipitate was collected by filtration, washed with dry ether (10 mL), and dried over $P_4O_{10}$ to afford crude product, which was further recrystallized from ethanol (21 mL) to afford an analytical sample of **32** (0.662 g, 58%): mp 126–127 °C; IR (KBr) 1459, 1220, 850, 745 cm$^{-1}$. Anal. Calcd for $C_9H_{14}O_4NP\cdot 0.5H_2O$: C, 45.86; H, 6.21; N, 5.95. Found: C, 45.95; H, 6.04; N, 5.96.

**Registry No. 1**, 1795-31-9; **2**, 3663-52-3; **3a**, 78-95-5; **3b**, 598-31-2; **3c**, 23479-35-8; **3d**, 4091-39-8; **3e**, 10409-46-8; **3f**, 683-50-1; **3g**, 917-93-1; **3h**, 532-27-4; **3i**, 70-11-1; **3j**, 4209-02-3; **3k**, 105-39-5; **3l**, 105-36-2; **3m**, 65868-37-3; **3n**, 70-23-5; **3o**, 76600-03-8; **4a**, 68064-25-5; **4d**, 68064-26-6; **4f**, 76600-04-9; **4g**, 76600-05-0; **4i**, 65868-38-4; **4j**, 65868-39-5; **4k**, 65868-40-8; **5a**, 57222-19-2; **5h**, 57222-17-0; **5j**, 65868-41-9; **5m**, 65868-42-0; **6a**, 65868-43-1; **6b**, 65868-44-2; **6c**, 65868-45-3; **6d**, 65868-46-4; **6e**, 65868-47-5; **6f**, 65868-48-6; **6g**, 65868-49-7; **6m**, 65868-50-0; **6n**, 66119-35-5; (*E*)-**9**, 76600-06-1; (*Z*)-**9**, 76600-07-2; **11**, 13716-45-5; **12**, 39059-59-1; **13a**, 76600-08-3; **13d**, 76600-09-4; **13f**, 76600-10-7; **14a**, 76600-11-8; **17a**, 65868-51-1; **17g**, 76600-12-9; **20a**, 76613-01-9; **21d**, 76600-13-0; **21f**, 76600-14-1; **21g**, 76600-15-2; **22a**, 73519-29-6; **22d**, 76291-02-6; **22f** (isomer 1), 76600-16-3; **22f** (isomer 2), 76600-17-4; **23a**, 1445-84-7; **23d**, 17151-59-6; *cis*-**23f**, 25030-59-5; *trans*-**23f**, 66187-63-1; **24**, 867-17-4; **26a**, 5954-28-9; **26d**, 76600-18-5; **26f**, 34600-14-1; **28a**, 65868-53-3; **28b**, 65868-55-5; **28f**, 65868-57-7; **29**, 70334-78-0; **30**, 65868-58-8; **31**, 76600-19-6; **32**, 65868-60-2.

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# Aromatic Oxidation with Peroxydiphosphate Catalyzed by Metal Ions[1]

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Aqueous potassium peroxydiphosphate brings about aromatic ring hydroxylation of benzene and toluene in modest yields in the presence of suitable metal ion oxidants, notably cupric ion. The acidity function ($-H_0$) of the reaction solution for the optimum conditions is −1.5–0, i.e., 0.05–1 M $H^+$, on the basis of a plot of total product yield vs. $-H_0$. The selectivity of ring hydroxylation increases with decreasing acidity of the aqueous solution and with increasing concentration of $Cu^{2+}$. But the reverse is true for the total product yield under these conditions. Our observations are consistent with a scheme by which the radical $H_2PO_4\cdot$ oxidizes the aromatic to a radical cation, similar to the mechanism suggested for aromatic hydroxylation by sulfate radical $SO_4^{-}\cdot$.

The reactions of phosphate radicals ($H_2PO_4\cdot$, $HPO_4^{-}\cdot$, $PO_4^{2-}\cdot$) with organic compounds in an aqueous solution have been extensively studied, where the rate constants for the consumption of radicals were measured[2-7] and the radical species produced during these reactions were identified.[7-11] Furthermore, the oxidation powers of phosphate radicals were measured for hydrogen atom abstraction and compared with those of $SO_4^{-}\cdot$ and $HO\cdot$.[12] But no information is available on the products formed by the reactions of these phosphate radicals with organic compounds.

The aromatic hydroxylation using radicals derived from Fenton's reagent ($Fe^{2+}$–$H_2O_2$) and peroxydisulfate ($Fe^{2+}$–$S_2O_8^{2-}$) has been studied. The latter reaction proceeds probably by a mechanism involving an electron transfer from the aromatics to sulfate radical, i.e., to form the radical cation of the aromatics.[13,14]

**Table I. Hydroxylation of Benzene with Peroxydiphosphate at 25 °C[a]**

| | | % yield | |
|---|---|---|---|
| [H⁺], M | $-H_0$[b] | PhOH | PhPh[c] |
| 8.18 | 2.16 | 4.0 | |
| 5.45 | 1.25 | 12.3 | trace |
| 3.48 | 0.78 | 18.7 | 3.9 |
| 1.82 | 0.26 | 18.5 | 24.8 |
| 1.00 | −0.13 | 16.1 | 42.0 |
| 0.87 | −0.17 | 19.1 | 36.9 |
| 0.46 | −0.50 | 9.2 | 53.1 |
| 0.33 | −0.81 | 10.3 | 45.4 |
| 0.087 | −1.19 | 9.1 | 47.1 |
| 0.050 | −1.43 | 3.0 | 28.4 |
| 0.020 | −1.72 | 0.1 | 8.3 |
| 0.010 | −2.04 | - | 5.0 |

[a] All runs were conducted by addition of 0.05 M $Fe^{2+}$ to a two-phase system containing $1.06 \times 10^{-2}$ M $H_2P_2O_8^{2-}$ and 0.5 M substrate at 25 ± 1 °C. Yields are based on $H_2P_2O_8^{2-}$ used. [b] Hammett acidity function.[d] [c] Based on $2C_6H_6 \longrightarrow C_{12}H_{10}$. [d] C. H. Rochester, "Acidity Functions", Academic Press, London, 1970.

On the other hand, the mechanism for the reactions of aromatic compounds with phosphate radicals is not definitive; i.e., Maruthamuthu et al. reported that there is no direct oxidative electron transfer from aromatic compounds to phosphate radicals in view of ESR studies[11] on one hand, but they reported that the substituent effect suggests an one-electron transfer from the aromatic ring to $H_2PO_4\cdot$ on the other.[6] Furthermore, no information about products in these reactions is obtained as stated above.

In the present paper, the reaction of aromatic compounds with phosphate radical derived by the reaction of

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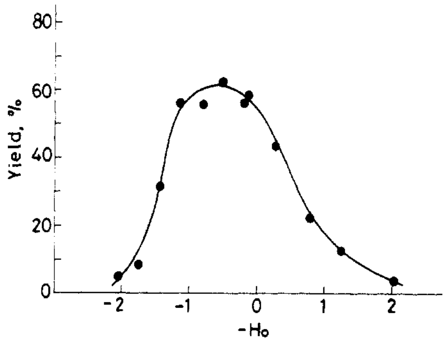


**Figure 1.** Effect of acidity on the product yield. The yields of phenol plus biphenyl are based on the peroxydiphosphate. $H_0$ is the Hammett acidity function.

peroxydiphosphate with metal ion ($Fe^{2+}$) was studied, especially for the product distribution together with the effects of acidity and catalyst nature on the yields. A probable mechanism will be discussed on the basis of the above data.

## Results and Discussion

**Benzene.** Firstly, the optimum conditions for aromatic hydroxylation in the peroxydiphosphate system were examined for the reaction of benzene with phosphate radical over a wide range of acidity in the absence of metal ion. The reaction was carried out by the slow addition of aqueous $Fe^{2+}$ to the system containing aqueous peroxydiphosphate and substrate in a two-phase system, where solutions were deaerated and oxygen displaced by $N_2$.

Figure 1 shows the effect of acidity on the yield; i.e., product yields (phenol plus biphenyl) were plotted against $-H_0$ (Hammett acidity function). Table I shows the yields of products.

As apparent from Figure 1 and Table I, the total yield was highest at $-H_0$ = -1.0–0; i.e., $[H^+]$ = 0.1–1 M; the yield was very poor outside these values of $H_0$, e.g., 5% at 0.01 M $H^+$ and 4% at 8.18 M $H^+$.

The yield of phenol is higher than that of biphenyl at high acidity (over 3.48 M $H^+$) (Table I), but at lower acidity the yield of phenol is lower than that of biphenyl.

In view of the dissociation constants of peroxydiphosphoric acid ($K_1 > 40$, $K_2 = 40$, $K_3 = 6.6 \times 10^{-6}$, and $K_4 = 2.1 \times 10^{-8}$)[15] the main attacking species may be $H_2P_2O_8^{2-}$ under our conditions. Peroxydiphosphate ion $H_2P_2O_8^{2-}$ is reduced by ferrous ion to phosphate radical ($HPO_4^{-}\cdot$) and phosphate ion,[16] eq 1.

$$H_2P_2O_8^{2-} + Fe^{2+} \rightarrow HPO_4^{-}\cdot + HPO_4^{2-} + Fe^{3+} \quad (1)$$

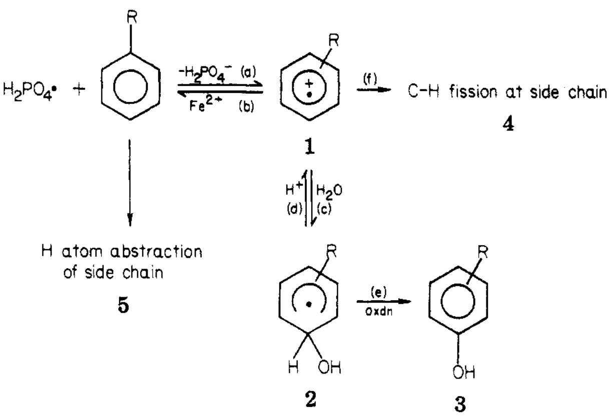
At the same time, the phosphate radicals exist in an acid dissociation equilibria,[12] (eq 2). Therefore, the phosphate radical may exist as a form of $H_2PO_4\cdot$ at the acidities of our experimental conditions of $H_0$ = -2–2.

$$H_2PO_4\cdot \underset{pK_1 = 5.7}{\overset{-H^+}{\rightleftharpoons}} HPO_4^{-}\cdot \underset{pK_2 = 8.9}{\overset{-H^+}{\rightleftharpoons}} PO_4^{2-}\cdot \quad (2)$$

Since phosphate radical $H_2PO_4\cdot$ is analogous to $SO_4^{-}\cdot$ in its nature,[12] the mechanism for the reaction of aromatic molecules with $H_2PO_4\cdot$ may be analogous to that of the peroxydisulfate suggested by Walling and co-workers[13,14] and shown in Scheme I.

Aromatic hydroxylation should be favored at lower acidity (path c) and high levels of $Cu^{2+}$ as an oxidant (path e), as will be discussed below.

Scheme I



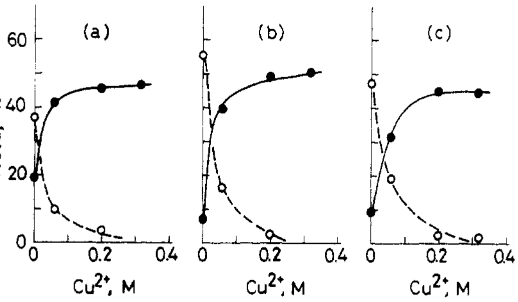


**Figure 2.** Effect of $[Cu^{2+}]$ on the product distribution of the oxidation of benzene with peroxydiphosphate: (a) $[H^+]$ = 0.87 M; (b) $[H^+]$ = 0.46 M; (c) $[H^+]$ = 0.087 M; (●) phenol; (○) biphenyl.

**Table II. Effect of Acidity on Oxidation of Toluene by Peroxydiphosphate**[a]

| $[H^+]$, M | $-H_0$[b] | % yield PhCH$_2$OH[c] | % yield cresol | % yield (PhCH$_2$)$_2$[d] |
|---|---|---|---|---|
| 3.48 | 0.78 | 16.9 (2.7) | | 23.0 |
| 1.82 | 0.26 | 14.2 (1.6) | | 34.0 |
| 0.87 | -0.17 | 7.4 | | 63.2 |
| 0.50 | -0.45 | 8.3 | | 55.0 |
| 0.33 | -0.81 | 2.8 | | 55.2 |
| 0.087 | -1.19 | 3.2 | | 42.3 |
| 0.050 | -1.43 | 3.3 | trace | 29.2 |
| 0.010 | -2.04 | 1.2 | 3.0 | 1.0 |

[a] Under the same conditions as shown in Table I unless noted otherwise. [b] Hammett acidity function. [c] Figures in parentheses indicate the yield of benzaldehyde. [d] Based on $2C_7H_8 \longrightarrow C_{14}H_{14}$.

Figure 2 shows the effect of $Cu^{2+}$ on the product distribution at various acidities. As apparent from the figure, the addition of $Cu^{2+}$ changed the distribution remarkably; e.g., at 0.46 M $H^+$ the yield of phenol was 6.9% in the absence of $Cu^{2+}$ but increased to 50.1% at 0.32 M $Cu^{2+}$, whereas the yield of dimer fell to a trace as 0.32 M $Cu^{2+}$. The same trend was observed at other acidities. The yield of phenol at the optimum conditions (0.46 M $H^+$, 0.32 M $Cu^{2+}$) was 50.1%, which is a lower value than that of peroxydisulfate oxidation (64%).[14]

**Toluene.** Toluene was used as a substrate to ensure Scheme I and to examine the possibility of the direct H atom abstraction from side chain by $H_2PO_4\cdot$. Table II shows the effect of acidity on the product yields in the absence of $Cu^{2+}$. Figure 3 shows the effect of $Cu^{2+}$ on product distribution. Similar acidity effects were observed with benzene and toluene; i.e., the total product yield was highest at $-H_0$ of -1–0, (0.1–1 M $H^+$). A decrease of the acidity always lowers the yield of benzyl alcohol, while that

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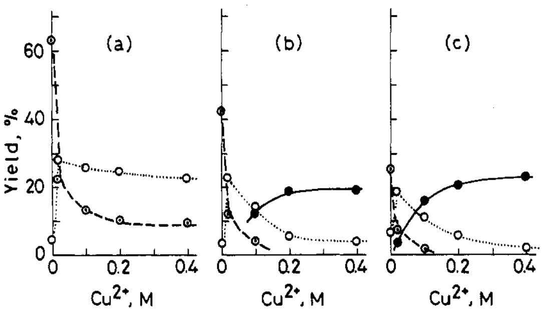

**Figure 3.** Effect of [$Cu^{2+}$] on the product distribution of the oxidation of toluene with peroxydiphosphate: (a) [$H^+$] = 0.87 M; (b) [$H^+$] = 0.087 M; (c) [$H^+$] = 0.050 M; (●) cresol; (○) benzyl alcohol; (⊙) bibenzyl.

of bibenzyl is highest (50–60%) at 0.5–1.0 M $H^+$ and it decreases at lower acidities. No formation of cresol was observed at high acidity (over 0.1 M $H^+$), while a small amount of cresol was detected at lower acidity (0.01–0.05 M $H^+$ Table II). The fact that low acidity favors the formation of cresol (aromatic hydroxylation) supports its formation via path c (Scheme I).

As shown in Figure 3, the addition of $Cu^{2+}$ at high acidity (0.87 M $H^+$) decreases significantly the total product yeild from 67.9% to 32.3% without formation of cresol. This observation shows that the high acidity favors the reverse of path c (i.e., path d), returning to 1. On the other hand, an increase in the concentration of added $Cu^{2+}$ decreases the extent of the C–H fission of the side chain in radical cation 1, also lowering the total product yield. This phenomenon may be due to the reduction of radical cation 1 to starting material by $Cu^+$ produced from $Cu^{2+}$.

At low acidities (0.087 M $H^+$ and 0.05 M $H^+$), an increase in the concentration of $Cu^{2+}$ significantly changed the product distribution; i.e., the formation of dimer was completely suppressed and that of benzyl alcohol was also lowered, whereas ring hydroxylation was promoted markedly; i.e., the yield of cresol was 23.2% at the optimum conditions (0.05 M $H^+$ and 0.40 M $Cu^{2+}$). The acidity in this case (0.05 M $H^+$) is lower than that (0.46 M $H^+$) at the optimum conditions for the formation of phenol in benzene hydroxylation, because the side chain fragmentation of benzene (Scheme I) is impossible.

The observed isomeric ratio of cresols was 66 (ortho):9 (meta):25 (para), the ratio being similar to those in peroxydisulfate (*o*:*m*:*p* = 62:5:33) and hydrogen peroxide hydroxylation (*o*:*m*:*p* = 59:12:29) under analogous conditions (0.05 M $H^+$ and 0.24 M $Cu^{2+}$).[14]

When $Fe^{3+}$ (0.20 M) was used in place of $Cu^{2+}$ as an oxidant, benzyl alcohol (5.5%), cresol (trace), and bibenzyl (23.1%) were obtained at 0.087 M $H^+$. This product distribution is remarkably different from that using $Cu^{2+}$ (0.20 M), where benzyl alcohol (5.7%), cresol (18.9%), and bibenzyl (trace) were formed. Therefore, $Cu^{2+}$ is an excellent catalyst for the aromatic hydroxylation and ferric ion favors the coupling of benzyl radicals. It is well-known that benzyl radical can easily couple to form bibenzyl in the presence of iron ion but not with copper ion.[17]

As stated above, the addition of $Cu^{2+}$ remarkably decreases the yields of bibenzyl and benzyl alcohol which are formed by H atom abstraction on the side chain and/or side-chain fragmentation of an intermediary radical cation (1). Therefore, this decrease in yields suggests that H atom abstraction in the side chain by $H_2PO_4\cdot$ (path g) is not important in this system, because $Cu^{2+}$ should not affect the H atom abstraction by $H_2PO_4\cdot$. Further, the formation of cresol alone at an excess of $Cu^{2+}$ at low acidities also suggests that $Cu^{2+}$ accelerates the oxidation of 2 (path e), which competes with C–H fission (path f). Thus, the equilibrium between 1 and 2 shifts to 2, i.e., hydroxylation of the radical cation 1 is accelerated.

Furthermore, slow addition of $H_2P_2O_8^{2-}$ to the system containing $Fe^{2+}$ and toluene (and also benzene) lowers the total yields by 30–40% compared with those observed in the reverse addition. This suggests the reduction of intermediate radical cations (1) with $Fe^{2+}$ present in excess of the starting material. Hence, it may be confirmed that the reaction of aromatic substances with $H_2PO_4\cdot$ proceeds via a radical cation as shown in Scheme I. As to the initial attack of $H_2PO_4\cdot$ on the aromatic ring, it is not clear whether it is a direct electron transfer from the aromatic to $H_2PO_4\cdot$ or an addition of $H_2PO_4\cdot$ to the ring followed by elimination of $H_2PO_4^-$.

Comparing the oxidation by $H_2P_2O_8^{2-}$ with that by $S_2O_8^{2-}$, the former reagent necessitates higher acidity than the latter to exert the same oxidizability; e.g., the oxidation of toluene with $S_2O_8^{2-}$ gave cresol (16%) and benzyl alcohol (12%) at $8 \times 10^{-5}$ M $H^+$ and $5 \times 10^{-3}$ M $Cu^{2+}$,[14] while the oxidation with $H_2P_2O_8^{2-}$ did not occur under these conditions. This may be due to the necessity of acid catalysts for the dissociation of the O–O bond for the $H_2P_2O_8^{2-}$–$Fe^{2+}$ system. In fact the iodometry of $H_2P_2O_8^{2-}$ at low acidities gave a lower value than that at high acidities.[16]

**Conclusion.** The oxidation of aromatic compounds by $H_2P_2O_8^{2-}$ proceeds via an intermediate radical cation 1 (Scheme I). The optimum acidity ([$H^+$]) for the oxidation was 0.1–1.0 M, but the optimum acidity for the aromatic hydroxylation was slightly lower. The observed isomeric ratio of hydroxylation of toluene by $H_2PO_4\cdot$ was similar to those by $SO_4^-\cdot$ and $HO\cdot$, indicative of the analogous electrophilic nature.

## Experimental Section

**Reagents.** Potassium peroxydiphosphate, dried under vacuum, has over 95% purity by iodometry. Other inorganic reagents (guaranteed grade) were used as received. Benzene (bp 80.1 °C) and toluene (bp 110.6 °C) were fractionated before use.

**Oxidations.** Reactions were started by a gradual addition of an aqueous solution of $FeSO_4$ to a stirred aqueous solution of the other reactants containing the aromatic substance, $K_4P_2O_8$, $H_2SO_4$, and $CuSO_4$ (or $Fe_2(SO_4)_3$). The reaction mixture was stirred vigorously under $N_2$ in a thermostatted bath maintained at 25 ± 1 °C. After completion of the reaction, the mixture was extracted with ether in four portions. The extract was dried, acetophenone was added as an internal standard, and the mixture was analyzed by GLC with FID, using a copper column packed with Silicone DC 550-KG 02 (2.5 mm × 2 m).

**Acknowledgment.** We thank Rasa Ind. Ltd. for their gift of potassium peroxydiphosphate.

**Registry No.** Benzene, 71-43-2; toluene, 108-88-3; dipotassium peroxydiphosphate, 27147-65-5; phenol, 108-95-2; biphenyl, 92-52-4; benzyl alcohol, 100-51-6; cresol, 1319-77-3; bibenzyl, 103-29-7; benzaldehyde, 100-52-7; $Fe^{2+}$, 15438-31-0; $Cu^{2+}$, 15158-11-9; $Fe^{3+}$, 20074-52-6.

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