Effects of Chelating Agents on the Preparation of Benzenediols by Oxidation of Phenol with Peracetic Acid

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The oxidation of phenol with peracetic acid has been investigated in connection with the industrial preparation of benzenediols. The effects of 25 additives, such as derivatives of monomeric and condensed phosphoric acid, chelating agents, and salts of polybasic carboxylic acids, were examined; derivatives of condensed phosphoric acid were found to be most effective. The oxidation of phenol (213 mmol) with peracetic acid (21 mmol) in the absence of the additives gave 1,2- and 1,4-benzenediols in only 5.8% and 7.6% yields, respectively. But in the presence of 2.0×10^{-7} mol of potassium diphosphate the yields of 1,2- and 1,4-benzenediol were 47% and 31%, respectively. The improvement in the yields by the additives is attributable to the masking of a trace of metals, especially iron and cobalt, present in the reaction mixture. These metals tend to catalyze the further oxidation of the benzenediols formed.

Benzenediols are important feedstocks in chemical industries and are extensively used as powerful reducing agents in the photography industry. 1,2-Benzenediol has been manufactured by means of alkali-fusion of 2-chlorophenol,[1] and 1,4-benzenediol by reduction of *p*-benzoquinone or by autooxidation of 1,4-bis(1-methylethyl)benzene.[2,3]

Preparation of benzenediols by oxidation of phenol with peroxides is important because it protects the enviroment from heavy metals or strong acid pollution. Many studies on this process have been described in patent applications.[4-9] On the other hand, the peroxy acid oxidation of phenol has been studied as a model reaction in the oxidative treatment of monomeric lignin[10] and in the metabolism of aromatic compounds *in vivo*.[11]

In cases of industrial preparation of benzenediols by oxidation of phenol with peracetic acid, it is recognized that the methods for the preparation of peracetic acid seriously affect the yields of benzenediols.[12] In order to suppress undesirable reactions such as the further oxidation of benzenediols, many additives have been tested:

1. Acids[6] (sulfuric acid, phosphoric acid, condensed phosphoric acids, hydrogen fluoride, and ion-exchanging resins of the sulfonic acid type);
2. Stabilizers for peroxides[12-14] (2,6-bis(hydroxymethyl)pyridine, 8-quinolinol, and dioctyl dihydrogendiphosphate);
3. Chelating agents[12-13] (iminodiacetate, nitrilo triacetate, ethylenediamine tetraacetate, citrate and tartarate); and
4. Vicinal benzenepolyols[9] (1,2-benzenediol and 1,2,3-benzenetriol).

This article describes the effects of both additives and metal ions.

Experimental

Materials. Peracetic acid was prepared by means of autooxidation of acetaldehyde in acetone by using 1,2,3,4-benzenetetracarboxlic acid as a catalyst.[15] After a stabilizer[14a] was added, acetaldehyde was evaporated and the residue was concentrated under a reduced pressure. After the addition of butyric acid, the solution was distilled under a reduced pressure (1.3 kPa) on a water bath of 30 °C. The distillate contained about 50 wt% of peracetic acid and acetic acid without water or hydrogen peroxide. This solution of peracetic acid can be stored in a refrigerator with no change for several months in the absence of stabilizers. This solution was diluted just before use with guaranteed grade acetic acid, and the concentration of peracetic acid was determined by iodometric titration.

Guaranteed grade phenol, glacial acetic acid, potassium diphosphate, and all other additives and metal salts except for octamethyldiphorphoric tetramide[16] were commercially supplied and used without purification.

General Reaction Procedure. Twenty grams (213 mmol) of phenol was stirred at 60 °C, under a nitrogen atmosphere, in a 100 ml two necked flask equipped with a dropping funnel and a thermometer. An acetic acid solution (11 ml) of peracetic acid (21 mmol) and an additive was added dropwise to the phenol through the dropping funnel within 10 min; the reaction mixture was kept at 60 °C for 2 h and then cooled in an ice water bath and analyzed by VPC. The conversion of phenol and the yields of benzenediols were all calculated based on the amount of peracetic acid used. Quinones and other further oxidized compounds were not analyzed.

Conditions of VPC Analysis. Phenol and 1,2- and 1,4-benzenediols were determined with a 1 m column packed with Tenax-GC at programmed temperatures from 150 °C to 200 °C (the rate of temperature increace; 6 °C min^{-1}); chlorobenzene was used as an internal standard and helium as a carrier gas (flow rate: 60 ml min^{-1}). The values of 1.0, 1.8, 6.6, and 8.5 min were observed as retention times of chlorobenzene, phenol, 1,2-benzenediol and 1,4-benzenediol, respectively.

Results and Discussion

The Oxidation in the Presence of Additives. Figure 1 illustrates a typical change in the conversion of phenol and in the yields of benzenediols as a function of the increasing amount of potassium diphosphate. As the amount of additive is increased, the total yield of benzenediols increased up to a constant value (Y_{max}), while the ratio of 1,2-benzenediol to the 1,4-isomer increased from 0.6 to 1.5. No improvement in the yields of benzenediols was observed with the addition of an amount larger than X_{max}, the amount of additive needed to get Y_{max}. From the industrial viewpoint, an additive with a greater Y_{max} and a smaller X_{max} is desirable. Figure 2 shows the effects of some additives on the total

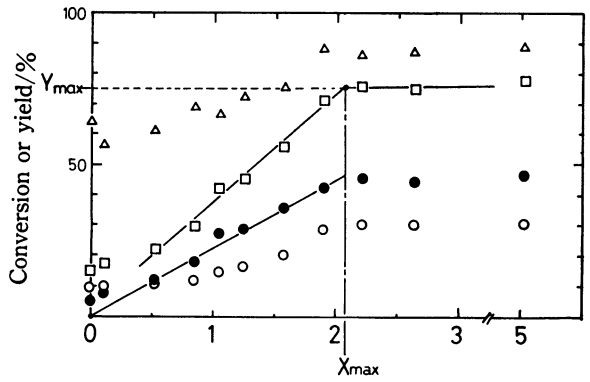

Fig. 1. Effects of potassium diphosphate on the conversion of phenol and the yields of 1,2- and 1,4-benzenediols.
△: Conversion of phenol, □: total yield of benzenediols, ●: yield of 1,2-benzenediol, ○: yield of 1,4-benzenediol. Phenol: 213 mmol, peracetic acid: 21 mmol, 60 °C, after 130 min.

yields of benzenediols.

Table 1 summarizes the X_{max}'s and Y_{max}'s of some additives tested. This table indicates the excellence of condensed phosphates as additives. For example, in the presence of 2.0×10^{-7} mol of potassium diphosphate, 9.6 mmol (47%) of 1,2-benzenediol and 6.6 mmol (31%) of 1,4-benzenediol were obtained, while in the absence of the additive, the yields of 1,2- and 1,4-benzenediol were only 1.2 mmol (5.8%) and 1.6 mmol (7.6%), respectively. Chelating agents, such as ethylenediamine tetraacetate and diethylenetriamine pentaacetate, were good additives. Derivatives of monomeric phosphoric acid and 1,2,3-benzenetriol were also good additives. The effects of diammonium hydrogenphosphate can be attributable to trace contaminants of

Table 1. Comparison of the effects of additives on the total yield of benzenediols[a)]

Additive	$X^{b)}_{max}$/mol	$Y^{c)}_{max}$/%
Sodium hexametaphosphate	9.1×10^{-8}	73
Sodium triphosphate	2.5×10^{-7}	73
Potassium diphosphate	1.85×10^{-7}	79
DTPA[d)]	3.9×10^{-7}	71
EDTA[e)]	1.4×10^{-6}	73
NTA[f)]	2.4×10^{-5}	73
Sodium imidobis(sulfate)	1.4×10^{-4}	50[g)]
1,2,3-Benzenetriol	5.2×10^{-4}	75
Diammonium hydrogenphosphate	1.1×10^{-6}	74
DMP-MMP[h)]	1.1×10^{-6}[i)]	74
Dimethyl phosphonate	1.1×10^{-3}	17[g)]
OMDPT[j)]	3.0×10^{-4}	64
Hexamethylphosphoric triamide	8.7×10^{-4}	29[g)]
Sodium malate	1.0×10^{-5}	34
Sodium citrate	8.2×10^{-5}	47
Sodium fumarate	9.4×10^{-5}	48
Sodium tartarate	1.7×10^{-5}	50
Acetylacetone	1.4×10^{-3}	52[g)]
8-Quinolinol	2.4×10^{-4}	43
Pyridine	3.1×10^{-4}	43
Sodium hydroxide	1.8×10^{-3}	34[g)]
Sodium borate	1.1×10^{-4}	26

a) Phenol: 213 mmol, peracetic acid 21 mmol, 60 °C, after 130 min. b) The smallest amount of additive needed for giving the maximum yields of benzenediols. c) The maximum total yield of benzenediols. d) Disodium trihydrogen diethylenetriamine pentaacetate. e) Disodium dihydrogen ethylenediamine tetraacetate. f) Sodium nitrilotriacetate. g) The maximum in the range tested. h) A 1 : 1 mixture of methyl dihydrogenphosphate and dimethyl hydrogenphosphate. i) Based on the average molecular weight. j) Octamethyldiphosphoric tetramide.

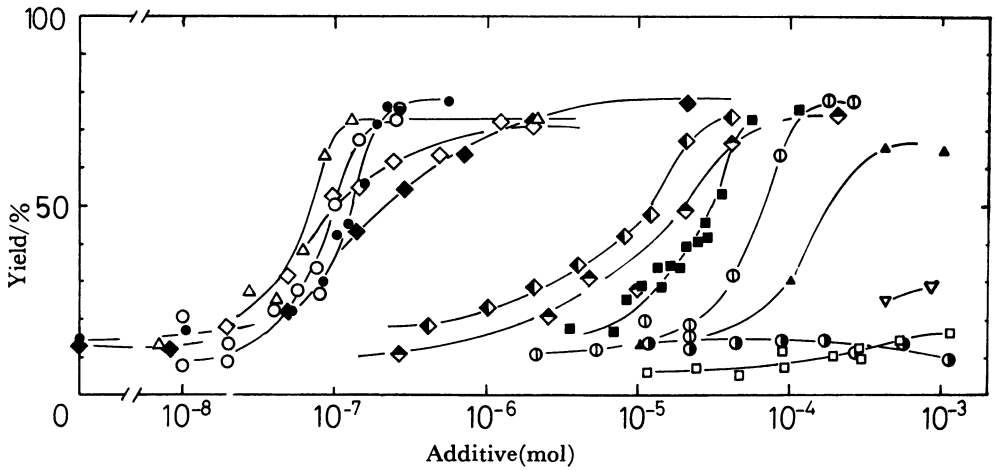

Fig. 2. Effects of some additives on the total yield of benzenediols.
△: Sodium hexametaphosphate, ○: sodium triphosphate, ●: potassium diphosphate, ■: diammonium hydrogen phosphate, ◑: 1 : 1 mixture of methyl and dimethyl phosphate, ▲: octamethyldiphosphoric tetramide, ▽: hexamethylphosphoric triamide, ◑: trimethyl phosphate, □: dimethyl phosphonate ◇: disodium trihydrogen diethylenetriamine pentaacetate, ◆: disodium dihydrogen ethylenediamine tetraacetate, ◐: sodium nitrilotriacetate, ◈: 1,2,3-benzenetriol. Phenol: 213 mmol, peracetic acid 21 mmol, 60 °C, after 130 min.

Table 2. Effects of the metals on the yields of benzenediols[a)]

Metal	Yields of benzenediols/%		
	1,2-	1,4-	Total
None	5.8	7.6	13.4
$Cr(OAc)_3 \cdot H_2O$	7.5	4.7	12.1
$Mn(OAc)_2 \cdot 4H_2O$	7.5	3.4	10.9
$Fe(NO_3)_3 \cdot 6H_2O$	0.2	4.4	4.6
$Co(OAc)_2 \cdot 4H_2O$	0.2	4.9	5.1
$Ni(OAc)_2 \cdot 4H_2O$	5.6	5.7	11.3
$Cu(OAc)_2 \cdot H_2O$	2.9	4.5	7.4
$Zn(OAc)_2 \cdot 2H_2O$	7.0	5.2	12.1
$K_3Fe(CN)_6$	3.2	5.1	8.3
$K_4P_2O_7$	45.8	30.6	76.4

a) Phenol: 213 mmol, peracetic acid: 21 mmol, 60 °C, after 130 min, in the presence of 2.4×10^{-7} mol of the salts.

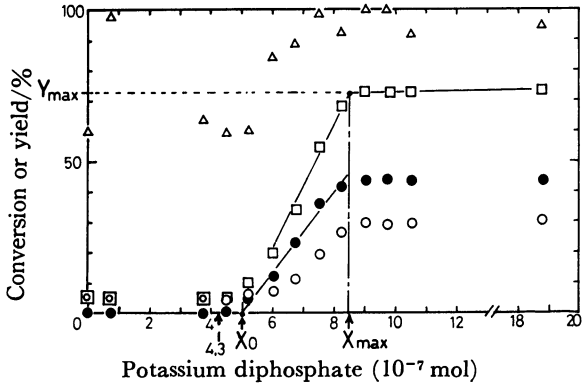

Fig. 3. Effects of potassium diphosphate on the conversion of phenol and the yields of 1,2- and 1,4-benzenediol in the presence of 4.3×10^{-7} mol of iron(III) nitrate.
△: Conversion of phenol, □: total yield of benzenediols, ●: yield of 1,2-benzenediol, ○: yield of 1,4-benzenediol. Phenol: 213 mmol, peracetic acid: 21 mmol, 60 °C, after 130 min.

derivatives of condensed phosphoric acid. This same effect is seen for a mixture of methyl dihydrogenphosphate and dimethyl hydrogenphosphate. On the other hand, bases, salts of organic polybasic acids, and ligating reagents such as acetylacetone and 8-quinolinol showed little effect. Crown ethers (15-crown-5, dibenzo-18-crown-6 and perhydrodibenzo-24-crown-8) were also tested, but they did not improve the yields of benzenediols.

These facts show that additives mask the effects of trace metal ions in the system.[17] The indicated additives with higher Y_{max} and lower X_{max} values mask the metal ions better.

The Oxidation in the Presence of Transition-metal Salts. The effects of transition-metal salts on the oxidation were tested. Table 2 shows that the addition of iron(II) or cobalt(II) salts depressed the yield of 1,2-benzenediol and had little effect on the yield of 1,4-benzenediol. On the other hand, the table also shows that salts of chromium(III), manganese(II), nickel(II), and zinc had little effect on the yields of both benzenediols.

In the presence of peracetic acid, transition-metal ions are in their higher oxidation states[18] and the benzenediols to be oxidized form complexes with these transition metal ions.[19-24] Therefore, it is reasonable that metal ions accelerate the further oxidation of benzenediols formed in this reaction.[25-27]

The Oxidation in the Presence of Both Potassium Diphosphate and a Transition-metal Salt. In order to clarify the relation between additives and metal ions in this system, phenol was oxidized in the presence of both diphosphate and a transition-metal salt.

Figure 3 illustrates the effect of potassium diphosphate on the conversion of phenol and the yields of 1,2- and 1,4-benzenediols in the presence of iron(III) nitrate (4.3×10^{-7} mol). In these cases, even upon increasing the amounts of potassium diphosphate up to X_0 (5.0×10^{-7} mol) no 1,2-benzenediol was obtained, and almost no change was observed in the yield of 1,4-benzenediol. Here X_0 means the smallest amount of potassium

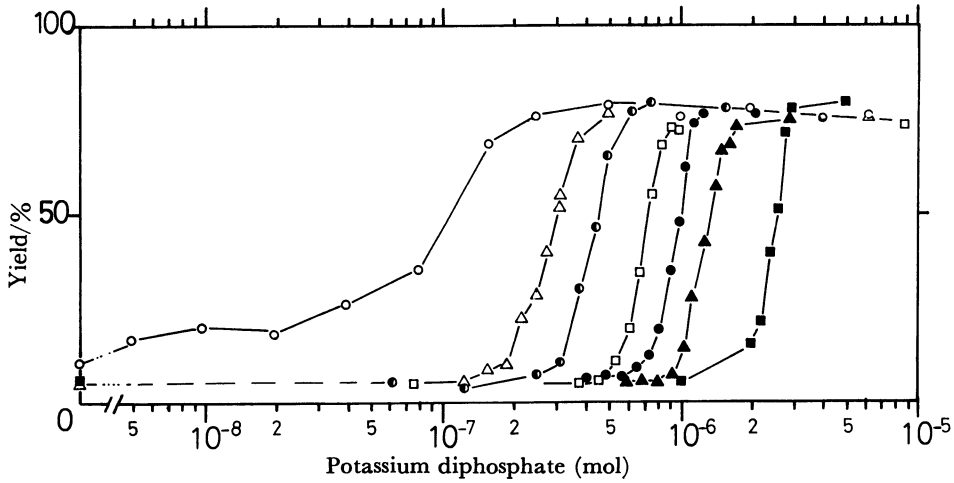

Fig. 4. Effect of potassium diphosphate in the presence of iron(III) nitrate on the total yield of benzenediols.
Iron(III) nitrate added: ○: nil, △: 1.1×10^{-7} mol, ◐: $21. \times 10^{-7}$ mol, □: 4.3×10^{-7} mol, ●: 6.4×10^{-7} mol, ▲: 8.5×10^{-7} mol, ■: 1.7×10^{-6} mol, phenol: 213 mmol, peracetic acid: 21 mmol, 60 °C, after 130 min.

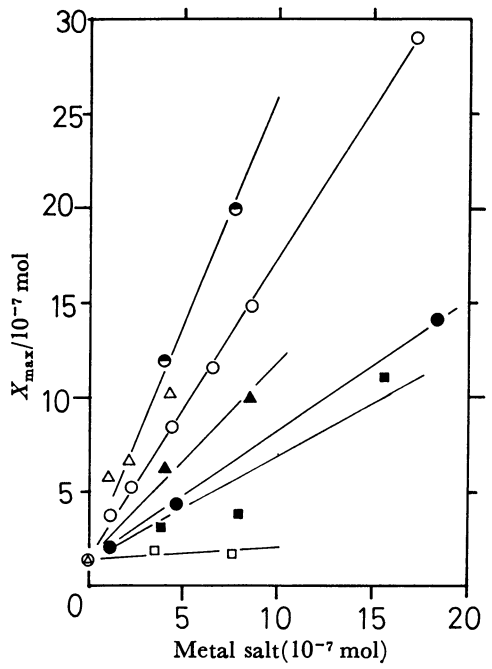

Fig. 5. Relation of X_{max} and the species and the amount of the metal salt added.
Metal salt: □: chromium(III) acetate, ▲: manganese-(II) acetate, ○: iron(III) nitrate, △: cobalt(II) acetate ■: nickel(II) acetate, ◓: copper(II) acetate, ●: zinc acetate. Phenol: 213 mmol, peracetic acid 21 mmol, 60 °C, after 130 min. X_{max}: the least amount of potassium diphosphate needed for giving the maximum yields of benzenediols.

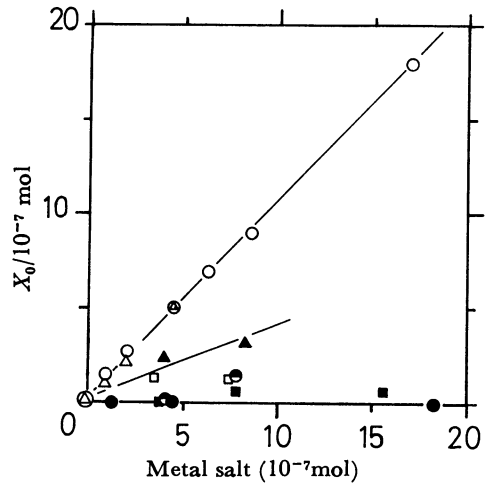

Fig. 6. Relation between X_0 and the metal salt added. X_0: The least amount of potassium diphosphate needed for giving 1,2-benzenediol (Notations and the conditions are the same as those in Fig. 5).

diphosphate needed for producing 1,2-benzenediol. The increase in the yields of benzenediols was observed with increasing amounts of diphosphate beyond X_0; the yields were saturated at the last stage.

Figure 4 shows the change in the total yield of benzenediols, in the presence of iron(III) nitrate (0—1.7×10^{-6} mol) and potassium diphosphate. The salts of cobalt and manganese exhibited the same kinds of feature, but the salts of chromium, nickel, copper, and zinc did not suppress the formation of 1,2-benzenediol. These findings are summarized in Figs. 5 and 6, which show that plots of X_{max}'s and X_0's against the amount of metal added are almost linear; their gradients are shown in Table 3.

Table 3. The gradients of the plots of X_{max}'s and X_0's against the amount of transition-metal salts added[a)]

Metal salts	$X^{b)}_{max}$/Metal	$X^{c)}_0$/Metal
Chromium(III)	0.1	0.13
Manganese(II)	1.01	0.35
Iron(III)	1.67	1.05
Cobalt(II)	2.05	1.16
Nickel(II)	0.63	0.04
Copper(II)	2.37	0.14
Zinc(II)	0.69	−0.18

a) Phenol: 213 mmol, peracetic acid: 21 mmol, 60 °C, after 130 min. b) The smallest amount of potassium diphosphate needed for giving the maximum yields of benzenediols. c) The smallest amount of potassium diphosphate needed for producing 1,2-benzenediol.

These findings support the explanation that these additives mask the metal ions contaminating the reaction mixture and that the presence of free metal ions, especially iron and cobalt, suppress the yields of benzenediols.

Quantitative Measurement of Metals Originally Present in the Reaction Mixture. After the reaction, X-ray flouresence was used to determine the concentration of iron in the reaction mixture; it was determined to be 180 mg m^{-3}. By flameless-atomic-absorption spectroscopy the concentrations of copper and cobalt were also determined to be 6.5 mg m^{-3} and less than 0.5 mg m^{-3}, respectively.

The intersections of the plots of X_{max}'s with the ordinate, in Fig. 5, correspond to the smallest quantitions of diphosphate needed for maximizing the yields of benzenediols when no metal was added. The amount of metal ions originally contained in the system can be estimated from this intersection and the gradients. This was calculated to be 173 mg m^{-3} if all of the metal contained was assumed to be iron; this value was in good agreement with that of 180 mg m^{-3} obtained from X-ray-fluorescence measurement.

On the basis of these findings, it is concluded that there was a trace of iron in the system, and that this catalyzed the further oxidation of benzenediols formed. The additives masking metal ions, consequently, improve the yields of benzenediols. From an industrial point of view, such a masking-reagent is useful for instant removal of these metal ions.

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