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$$R^1SOR^2 \xrightarrow{(R^3)_2CuLi} R^1SOR^2 \xrightarrow{(R^3)_2CuLi} R^1SR^3$$

17
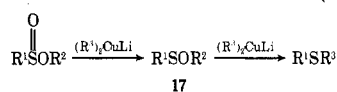
then react with the organometallic reagent. We are able to show that methyl phenylsulfenate (**17**, $R^1 = C_6H_5$; $R^2 = CH_3$) reacts rapidly and smoothly with $(CH_3)_2CuLi$ to give methyl phenyl sulfide in good yield. This, however, does not allow us to explain the anomous reactions that produce *n*-butyl phenyl sulfide.

(19) Phenyl *p*-tolylsulfinate ester could be prepared in good yield, as a colorless liquid which decomposed on standing overnight (at −20 °C) to give a brown tar. This observation is corroborated by Baarschers and Krupay, who attempted to obtain phenyl methylsulfinate (**4**, $R^1 = CH_3$; $R^2 = C_6H_5$).[20]
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(NMR) spectra were recorded on a Varian Associates T-60 spectrophotometer. All data are recorded in parts per million relative to Me₄Si (used as an internal standard). Mass spectra were recorded on an AEI-MS-902 mass spectrometer equipped with a direct insertion probe. Melting points were obtained on a Gallenkamp apparatus and are uncorrected. High-pressure liquid chromatography was performed with a Water's Associates ALC 202-/401 liquid chromatograph with a U6K injector and refractive index detector for preparative work. Microanalyses were performed by Organic Microanalyses, Montreal, Canada. Common intermediates were obtained from commercial sources and were purified as necessary.
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Enzymic-Like Aromatic Oxidations. Metal-Catalyzed Peracetic Acid Oxidation of Phenol and Catechol to *cis,cis*-Muconic Acid[1]

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Phenol is oxidized to *cis,cis*-muconic acid (CCMA) by peracetic acid in the presence of catalytic quantities of Cu(II) and Fe(III). No CCMA is formed in the absence of these metals or in the presence of other specified metals. The yield of CCMA depends on the kind and quantity of metal ion used, being higher for oxidations with Fe(III) than Cu(II). Trace quantities of Fe(III) are effective at catalyzing the formation of CCMA. Catechol has been identified as an intermediate in the reaction. Kinetic studies indicate that the rate of disappearance of phenol is independent of metal and first order in both phenol and peracetic acid. The results are accommodated by a scheme which involves hydroxylation of phenol to give a mixture of catechol and *p*-hydroquinone followed by the formation of a metal–catechol complex which is rapidly and cleanly oxidized to CCMA.

In 1931 Boeseken and Engelberts[2] reported the oxidative cleavage of phenol (**1**) to *cis,cis*-muconic acid (CCMA, **2**)[3]

1   **2**
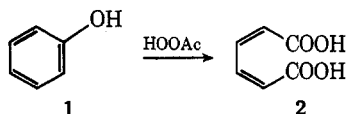
using peracetic acid (HOOAc). The carbon–carbon bond adjacent to the OH is cleaved leaving the stereochemistry about the two remaining double bonds unchanged. This reaction represents a rare example of a specific, nonenzymatic oxidative cleavage of an aromatic system. Other workers have since reported the peracetic acid oxidation of catechol[4] (**3**) to CCMA

**Table I. Fe(III)-Catalyzed HOOAc Oxidation of Phenol[a]**

[Phenol]$_0$/[Fe(III)][b]	Yield of CCMA, %
100	40
1 000	40
20 000	37
100 000	18
300 000	12
600 000	9
1 000 000	<7[c]

[a] These results are for oxidations carried out in 20 wt % HOOAc. The same results are obtained in 10 wt % HOOAc. [b] [Phenol]$_0$ = 0.92 M. [c] Limit of detectability.

Table II. Cu(II)-Catalyzed Peracetic Acid Oxidation of Phenol[a]

[Phenol]$_0$/[Cu(II)][b]	Yield of CCMA, %
100	24
1 000	24
2 000	18
3 000	11
5 000	<7[c]

[a,b,c] See corresponding footnotes in Table I.
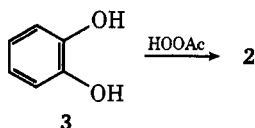
and the oxidation of other derivatives of phenol,[5] such as *p*-cresol, *p*-bromophenol, and *p*-chlorophenol, to the corresponding β-substituted muconic acids. In addition, catechol has been reportedly oxidized to *cis,cis*-muconic acid with molecular oxygen activated by copper(I) chloride.[6]

In a well-known enzymatic reaction, catechol is oxidized to CCMA by oxygen in the presence of pyrocatechase.[7] Our interest in this enzymatic oxygenation involving the iron-containing enzyme pyrocatechase led us to study the peracetic acid oxidation of phenol in the presence of Fe(III) and other metal ions. We were also particularly interested in the effects of copper since it is found in the enzyme phenolase which catalyzes the hydroxylation of phenol to catechol and also the oxidation of catechol to *o*-benzoquinone.[8]

Experimental Section

Melting points were determined on a Fisher-Johns apparatus and are uncorrected. NMR spectra were recorded on a Perkin-Elmer R12B and chemical shifts are expressed in parts per million (δ) downfield from internal tetramethylsilane: s = singlet, d = doublet, m = multiplet, etc. Mass spectra were recorded on a AEI MS-9 mass spectrometer, direct inlet, 70 eV. A Varian Model 635 visible-uv recording spectrophotometer was used to obtain uv spectra. VPC work was carried out with a Varian Aerograph Model 920 chromatograph (60 ml He/min). Atomic absorption work was carried out with a Perkin-Elmer 103 instrument.

Materials. The phenol used was Mallinckrodt analytical reagent or MCB, reagent. The acetic acid was Matheson Scientific, reagent. The peracetic acid was obtained from FMC Corp. as a 40 wt % solution in acetic acid solvent. Catechol was supplied by Eastman. The ferric acetate (purified powder basic) was obtained from City Chemical Corp. The cupric acetate monohydrate (reagent grade) was supplied by MCB and was found to contain 0.0007 wt % Fe as determined by atomic absorption analysis. All other metals employed in reactions were reagent grade and used as received.

General Procedure for Metal-Catalyzed Oxidations of Phenol in 10 and 20% Peracetic Acid. With the exception of varying the kind and quantity of metal used, the same procedure was followed for all phenol oxidations in 10 or 20% peracetic acid. The metal salt

was usually directly weighed out for use in a reaction. However, in oxidations where [phenol]$_0$/[metal] was > 1000 [in Cu(II) and Fe(III) oxidations, see Tables I and II], aliquots of standard solutions of the metal salt in acetic acid were used in order to accurately dispense the required quantity of metal.

The following procedure for the Fe(III)-catalyzed peracetic acid oxidation of phenol is typical of those oxidations carried out in 20% peracetic acid. Phenol (5.00 g, 0.0532 mol), glacial acetic acid (20.0 g), and basic ferric acetate (0.0104 g, 0.0000544 mol) were placed in a glass-stoppered 125-ml Erlenmeyer flask and stirred magnetically with a Teflon-coated stirring bar. After the ferric acetate was dissolved, a mixture of 10.5 g of acetic acid and 30.5 g of 40% peracetic acid (12.2 g, 0.161 mol HOOAc) was added from an addition funnel over a period of 5 min to the magnetically stirred phenol–Fe(III) solution. White *cis,cis*-muconic acid (CCMA) precipitated from solution as the reaction proceeded. After stirring at 25 °C for 5 days, the reaction mixture was cooled to about 10 °C and the product was collected by suction filtration, washed with 1 ml of cold water, and air dried to give 2.47 g of CCMA, mp 180 °C dec (lit.[9] 184 °C). The uv spectrum [λ_{max} (95% EtOH) 257 nm (ϵ_{max} 21 000)] of the product was identical with that previously reported[7] for CCMA. An NMR spectrum (CCl$_4$) of the dimethyl ester, dimethyl *cis,cis*-muconate, was identical with that previously reported[10] and showed the following absorptions: δ 3.68 (s, 6, carbomethoxy), 5.9 (m, 2, olefinic α to carbomethoxy), 7.9 (m, 2, olefinic β to carbomethoxy). The absence of absorptions at δ 7.28 and 6.15 indicated that no *trans,trans*-muconic acid was present in the product.[10] Purification of the product with aqueous sodium bicarbonate did not change the yield. The yield was corrected for the quantity of CCMA which was soluble under the reaction conditions. The solubility of CCMA was determined to be 9 mg/ml under conditions approximating those of the reaction.[11] Since the reaction volume was 59 ml, the observed yield was corrected by adding to it 0.52 g (7%) to account for the quantity of CCMA remaining in solution. The total corrected yield of CCMA is then calculated to be 2.99 g (40%). A corrected yield of 40% was also obtained in a Fe(III)-catalyzed oxidation in 10% HOOAc.

Oxidations carried out in the absence of metal or with the following metals gave no visible product: Ni(II), Co(II), V(0), Ag(I), Zn(II), Fe(II), Na(I), Hg(II), Cr(III), Mn(II). The reaction mixtures became very dark, essentially black, after 5 days at room temperature but no CCMA precipitated from solution in either 10 or 20% HOOAc oxidations. These results limit the yield of CCMA to <7%, which corresponds to the solubility of CCMA in 20% HOOAc solutions.

Stability of Fe(III)–HOOAc Solutions. The reaction was carried out as described above for oxidations with 20% HOOAc, except that no phenol was added. Basic ferric acetate (0.0101 g, 0.0000529 mol) was used as the source of Fe(III). Samples of reaction mixture (0.5–0.7 g) were withdrawn periodically, accurately weighed, and iodometrically analyzed using a 0.1 M standardized sodium thiosulfate solution and starch indicator. The wt % HOOAc was calculated as a function of time and found to be the following: 22.0 ± 0.5% (0 day), 21.5 (4 days), 20.7 (6 days), 20.0 (8 days), 18.0 (13 days), 16.7 (18 days).

Metal-Catalyzed Peracetic Acid Oxidations of Catechol. The following Fe(III)-catalyzed oxidation illustrates the general procedure for catechol oxidations. To a magnetically stirred solution of 10.5 g of HOAc, 30.5 g of 40% HOOAc (12.2 g, 0.161 mol HOOAc), and 0.0106 g (0.0000554 mol) of ferric acetate in a glass-stoppered 125-ml Erlenmeyer flask was slowly added, dropwise over a period of 7–9 h from a micrometer addition funnel, a solution of 5.90 g (0.0537 mol) of catechol in 20.0 g of acetic acid. The entire reaction was carried out under a nitrogen atmosphere over a 5-day period. The CCMA precipitated from solution as the reaction proceeded. The product was isolated in the same manner described above for phenol oxidations yielding 3.83 g of CCMA. Purification with aqueous NaHCO$_3$ did not change the yield. The observed yield was corrected by adding 0.52 g for the solubility of CCMA in the reaction medium as previously discussed. The total corrected yield of CCMA was then calculated to be 4.35 g (58%). After comparing a number of runs, it was found that the yield depended on the rate of catechol addition and varied from 45 to 65%. Too fast or too slow an addition cut the yield, with the optimum addition time being 7–9 h. Since it was difficult to reproduce the addition rate, the yield of CCMA varied from run to run.

Similar results were obtained with Cu(II) as the catalyst; however, the yields of CCMA were lower and varied from 20 to 40%. A small yield (<0.2 g) of CCMA was obtained in an oxidation of catechol carried out in the absence of metal.

Intermediates in Phenol Oxidations. The procedure described above for phenol oxidations in 20% HOOAc was followed. The following analysis was carried out for oxidations with Cu(II), Fe(III), and no metal. A 5-ml aliquot of reaction mixture was removed after ap-

proximately 20 h of reaction and was treated with aqueous sodium sulfite to reduce any peroxides present.[12] Sufficient saturated, aqueous sodium bicarbonate was added to neutralize the solution, after which it was continuously extracted with ether for 24 h. The ether layer was dried with magnesium sulfate and the solvent evaporated, leaving an oily residue which was dissolved in a small amount of ether and analyzed by VPC. A 3% SE-30 on 100–120 Varaport 30, 5 ft × 0.25 in. stainless steel column was used. The temperature was varied. The retention times of catechol and p-hydroquinone were 2.2 and 3.6 min, respectively, at 125 °C. Both catechol and p-hydroquinone were identified by their retention times and coinjection with authentic samples. In one analysis of an uncatalyzed oxidation, the catechol peak was collected by VPC and a mass spectrum recorded which was identical with that of an authentic sample.

Kinetic Method. The disappearance of phenol was followed by VPC for oxidations with Fe(III), Cu(II), and no metal at 25 °C in 20% peracetic acid according to the general procedure previously described. The molar ratio of phenol to metal catalyst was 1000 for Fe(III) and 100 for Cu(II) oxidations. The VPC method consisted of quenching 5-ml aliquots of reaction mixture at various times by treatment with aqueous sodium sulfite to reduce all peroxides present. After sufficient aqueous sodium bicarbonate was added to neutralize the solution, it was continuously extracted with ether for at least 24 h. The ether layer was dried with magnesium sulfate and the solution evaporated. An accurately weighed sample of naphthalene was added to the residue as an internal standard, and the mixture was dissolved in a few milliliters of ether. A sample was analyzed by VPC (column 3% SE-30 on 100–120 Varaport 30, 5 ft × 0.25 in. stainless steel, T = 85 °C, retention time of phenol 2.0 min, retention time of naphthalene 5.8 min), and the areas of phenol and naphthalene were determined. VPC analysis of a standard solution containing equimolar quantities of phenol and naphthalene indicated that the ratio of the area of hydrocarbon to phenol was 1.21:1. The concentration of phenol as a function of time was calculated from the VPC data, and a plot of [phenol]$^{-1}$ vs. time was made for each run. Second-order rate constants were obtained from the slopes of the best straight lines through the data points.

Results

The balanced reaction (below) for the oxidation of phenol to CCMA requires 3 mol of peracetic acid per mole of phenol.
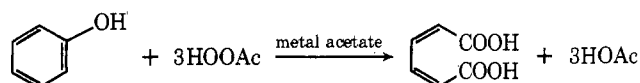
Reactions were carried out in the presence of various metal acetate salts at room temperature in 10 or 20 wt % peracetic acid in acetic acid solvent employing stoichiometric quantities of reactants. The concentrations were 0.46 M phenol, 1.39 M HOOAc in 10% HOOAc runs, and 0.92 M phenol, 2.78 M HOOAc in 20% HOOAc runs. The metal and the quantity used were varied. Reactions were carried out for 5 days at 25 °C; less than 2% phenol remained after this time in oxidations carried out in 20% peracetic acid.

Contrary to the earlier reports of Boeseken and Engelberts[2] and others,[5] we have found that CCMA is not formed in the absence of metal. The oxidation of phenol with peracetic acid leads to a complex mixture of products resulting from the oxidative degradation of quinones and polyhydroxylated aromatics formed during the course of the reaction. Two metal ions, Fe(III) and Cu(II), have been found to effectively promote the formation of CCMA. After examining our data, it is reasonable to conclude that the results of earlier workers were due to trace metal impurities, probably Fe, in their chemicals or equipment.

The results of oxidizing phenol with peracetic acid in the presence of Fe(III) are summarized in Table I. It is clear from these results that very small quantities of Fe(III) are effective in promoting the formation of CCMA, and that the yield of CCMA depends on the quantity of Fe(III) present. A maximum yield of 40% CCMA is obtained when the molar ratio of phenol to Fe(III) is 1000. The yield does not increase when the amount of Fe(III) is increased to a ratio of 100:1. As the molar ratio of phenol to Fe(III) is increased, and, hence, the quantity

of Fe(III) decreased, the yield of CCMA decreases and essentially goes to zero at ratios greater than 1 000 000:1. Fe(0) was also found to catalyze the formation of CCMA. A yield of 36% CCMA was obtained in a reaction in which iron filings were used as the catalyst; the molar ratio of phenol to Fe(0) was 100. An attempted oxidation with Fe(II) led to the violent decomposition of the peracetic acid probably via a free-radical process.

Ferric acetate was used as the source of Fe(III) in all reactions listed in Table I. The same results were obtained using ferric chloride, which indicates that the reaction is independent of the source of Fe(III).

The rate of decomposition of peracetic acid was measured in the absence of phenol to determine if the Fe(III)–HOOAc solutions were stable. The conditions were identical with those employed in runs where the ratio of phenol to Fe(III) was 1000 except the phenol was not included. The extent of decomposition was found to be less than 2 wt % over a period of 5 days indicating the Fe(III)–HOOAc mixtures to be relatively stable in the absence of phenol.

Reactions carried out under nitrogen gave the same results indicating that the presence of oxygen does not affect the course of the reaction.

The results summarized in Table II indicate that Cu(II) is less effective than Fe(III) in promoting the formation of CCMA. A maximum yield of 24% is obtained when the molar ratio of [phenol]$_0$/[Cu(II)] is 100. As with Fe(III), the yield of CCMA is dependent on the concentration of Cu(II), decreasing to essentially zero when the phenol to Cu(II) ratio is 5000. The phenol/Cu(II) ratio was not decreased below 100, since higher Cu(II) concentrations lead to appreciable decomposition of peracetic acid.

In order to determine if the results with Cu(II) were indeed due to Cu(II) and not Fe(III) impurities, the cupric acetate employed in the Cu(II) oxidations was analyzed by atomic absorption and found to contain 0.0007 wt % Fe. This quantity of iron would give a phenol/Fe ratio of 3.8×10^7 in a Cu(II)-catalyzed run in which the phenol/Cu(II) ratio was 1000. Hence, there is insufficient Fe impurity in the cupric acetate to account for the results in Table II, confirming that Cu(II) is the catalyst.

Catechol and p-hydroquinone were found to be present in metal-catalyzed reactions as well as in reactions containing no metal. In all cases, these compounds were present in very small quantities (<1% of total material balance) throughout the oxidations. Both were identified and isolated from reaction mixtures by VPC. The relative quantities of these substances detected under various conditions were as follows: no metal, p-hydroquinone $\simeq$ catechol; Cu(II), p-hydroquinone > catechol; Fe(III), p-hydroquinone and no catechol. The absence of detectable quantities of catechol in Fe(III) oxidations is particularly noteworthy.

Kinetic studies indicate that the rate of disappearance of phenol is independent of metal (Figure 1); i.e., *phenol disappears at the same rate whether metal is present or not.* A second-order plot of the data[13] gives a good straight line indicating that the reaction is second order overall, first order each in phenol and peracetic acid.[14] The measured rate constant for the disappearance of phenol at 25 °C is $3.4 \pm 0.4 \times 10^{-2}$ M^{-1} h^{-1}.

We have oxidized catechol to CCMA with peracetic acid in the presence of Fe(III) in 50–60% yield.

$$3 + 2\text{HOOAc} \xrightarrow{\text{Fe(III)}} 2 + 2\text{HOAc}$$
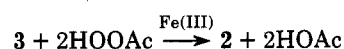
Very small amounts (<3%) of CCMA were formed when the oxidation was carried out in the absence of Fe(III). To carry out a successful oxidation, it is essential that the catechol be introduced to a mixture of metal and peracetic acid in such
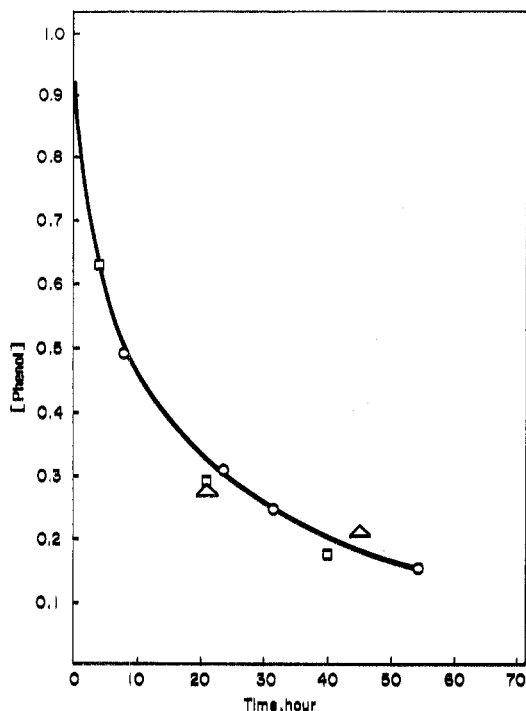
Figure 1. Plot of [phenol] vs. time for oxidations of phenol with peracetic acid in the presence of Fe(III), O; Cu(II), □; and no metal, Δ. These data represent 84% reaction.

a manner that it is always kept at a very low concentration to simulate the conditions under which the catechol is produced and converted to CCMA in the phenol oxidations. Mixing all the reactants at once leads to a black solution and no CCMA.

Discussion

Our results lead us to postulate the following scheme for the metal-catalyzed peracetic acid oxidation of phenol.
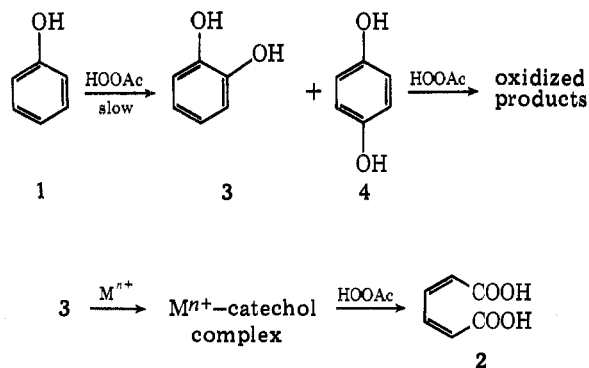
The first step involves hydroxylation of phenol to give a mixture of catechol (**3**) and *p*-hydroquinone (**4**). Both of these compounds were identified in reaction mixtures. The first step is rate determining and independent of metal as indicated by the kinetic results and supported by the observation that **3** and **4** are found in uncatalyzed as well as catalyzed reactions. In the presence of Fe(III) or Cu(II), it is proposed that catechol forms a complex with the metal which is rapidly and cleanly oxidized to CCMA. The observation that small quantities of metal give relatively large amounts of CCMA indicates the catalytic nature of the reaction and further supports the idea that the oxidation of the complex is relatively fast.

In the absence of Fe(III) or Cu(II), and as a competing reaction in the presence of these metals, catechol and *p*-hydroquinone are oxidized and degraded to give products other than CCMA. For example, **3** and **4** may be oxidized to qui-

nones or further hydroxylated to give polyhydroxylated aromatics and then degraded as observed by other workers[15] under similar conditions. The formation of the red molecular complex phenoquinone[16] has been observed in our reaction. It results from the oxidation of *p*-hydroquinone to *p*-benzoquinone which then combines reversibly with 2 mol of phenol to form the complex. Phenoquinone is highly dissociated under our conditions, and we estimate that no more than 1% of the phenol is tied up in this complex at any time during the reaction. The stepwise formation of *p*-benzoquinone and phenoquinone could be observed in the oxidation of phenol by a change in the color of the reaction mixture from clear to yellow (*p*-benzoquinone) and then to red (phenoquinone) as the reaction proceeded.

The hydroxylation of phenol and other activated aromatic compounds employing reagents such as H_2O_2-$AlCl_3$,[17] H_2O_2-HF,[15] and CF_3CO_3H[18,19] have been reported. Vesely and Schmerling obtained a mixture of 56% *p*-hydroquinone and 44% catechol on hydroxylating phenol with H_2O_2-HF at room temperature. In our reaction only catechol is oxidized to CCMA, and, hence, the maximum yield of CCMA that we could expect, using the results of Vesely and Schmerling as a model for our first step, is about 44% of theoretical. Thus our yields of 24 and 40%, based on phenol, actually correspond to 55 and 91% based on the maximum amount of catechol that could form in the first step using the data of Vesely and Schmerling for the hydroxylation of phenol with H_2O_2-HF.

If the oxidation of a catechol-metal complex leads to CCMA, then it should be possible to oxidize catechol to CCMA in the presence of Fe(III) and Cu(II). As reported earlier in this paper, we have oxidized catechol to CCMA with peracetic acid in the presence of Fe(III) and Cu(II).

The postulation of a metal-catechol complex as an intermediate in the phenol oxidation is reasonable in light of the observation that phenol is not oxidized to CCMA in the absence of Fe(III) or Cu(II) in spite of the fact that catechol is formed in the absence of these metals.[22b] Thus it appears that the role of Fe(III) and Cu(II) is to provide a reaction path whereby catechol can be oxidized to CCMA with little or no side reaction. In the absence of these metals, catechol is probably oxidized to products other than CCMA since the "directing" effect of the metal is absent. This interpretation is consistent with our observation and those of Vesely and Schmerling who found that the oxidation of catechol with hydrogen peroxide leads to complex reaction mixtures containing tri- and tetrahydroxylated benzene and products derived from these polyhydroxylated aromatics.[15]

Metal-catechol complexes of the type ML^{n-2}, ML_2^{n-4}, and ML_3^{n-6} ($M^{n+} = Fe^{3+}$ or Cu^{2+}, H_2L = catechol) are reasonable to postulate.[20-22] Cu(II) can form complexes with one or two catechol ligands whereas Fe(III) can coordinate to as many as three catechols. It is interesting to note that a relatively stable salt of CuL_2^{2-} has been prepared.[23,24]

A comparison of stability constants for Fe(III) and Cu(II) complexes with catechol indicates that Fe(III) forms the more stable complex. The log of the stability constant for CuL is 13.8[21a,c,22,25] while that for FeL+ is 20.9.[26] None of the other metals used in our studies have log stability constants for ML^{n-2} greater than about 8.[21]

Our results strongly suggest that a correlation exists between the ability of a metal to catalyze the formation of *cis,cis*-muconic acid and the stability of the metal-catechol complex. Fe(III)-catechol complexes are among the most stable metal-catechol complexes known.[21] We feel that this is the reason Fe(III) is more effective than other metals in catalyzing the formation of *cis,cis*-muconic acid. The fact that Cu(II) forms a less stable complex with catechol than Fe(III), but a more stable complex than the other metals used in this study, is consistent with it giving a yield of *cis,cis*-muconic

acid intermediate between that of Fe(III) and the other metals.

The idea that Fe(III) is more effective than Cu(II) in removing free catechol from the reaction mixture, and thus increasing the yield of *cis,cis*-muconic acid, is supported by our observation that no detectable quantity of catechol is present during the course of the reaction (as determined by VPC) in oxidations containing Fe(III) whereas detectable quantities are present in Cu(II) oxidations. If the ratio of metal–ligand complex to free metal is calculated under the reaction conditions using the formation constants cited in the previous paragraph for Cu(II) and Fe(III), one finds the ratio $[CuL]/[Cu^{2+}] \simeq 10^{-7}$ and $[FeL^+]/[Fe^{3+}] \simeq 10^0$ indicating that Fe(III) is approximately 10^7 times more effective in coordinating to catechol than Cu(II) under the reaction conditions.[27]

There are several mechanisms possible for the proposed oxidation of the metal–catechol complex. One possibility could involve a concerted electron transfer from the ligand through the metal to coordinated HOOAc molecules.

electron flow
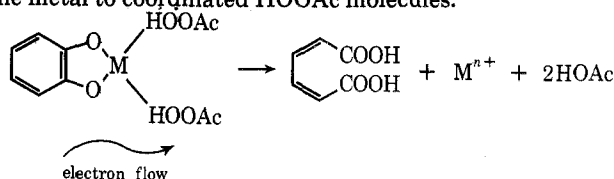
Another scheme could involve a stepwise oxidation of the metal–catechol complex through *o*-benzoquinone in a manner similar to that postulated for the oxidation of catechol to *o*-benzoquinone by the Cu(II)-containing enzyme phenolase.[8]

The relationship between the Fe(III) and Cu(II)-catalyzed peracetic acid oxidations of phenol as reported in this paper and the corresponding enzymatic oxidations of catechol and phenol by the iron-containing enzyme pyrocatechase and the copper-containing enzyme phenolase is very apparent. We believe that our reaction may serve as a useful model for these enzymatic oxygenations, and therefore we are continuing our work in an effort to further elucidate the mechanism of the metal-catalyzed phenol oxidation in the hope that it may shed more light on the corresponding enzymatic processes.

Registry No.—Peracetic acid, 79-21-0; phenol, 108-95-2; Cu(II), 15158-11-9; Fe(III), 20074-52-6; *cis,cis*-muconic acid, 1119-72-8; dimethyl *cis,cis*-muconate, 1119-43-3; catechol, 120-80-9.

References and Notes

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(3) The following abbreviations are used throughout the paper: CCMA, *cis,cis*-muconic acid; HOOAc, peracetic acid; HOAc, acetic acid.
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(11) It is difficult to accurately determine the "solubility" of CCMA under the reaction conditions since the composition of the solvent changes as the reaction proceeds. The value of 9 mg/ml is our best estimate of the solubility under the reaction conditions as determined from solubility measurements in a variety of solvents ranging from pure acetic acid to 20 wt % peracetic acid in acetic acid solvent. The solubility factor includes any CCMA which disappears as a result of reaction with peracetic acid. It should be noted that the interpretation of our results does not depend on the exact value used for the solubility since we are comparing yields obtained under identical conditions.
(12) Sodium sulfite reduces any *p*-benzoquinone and *o*-benzoquinone present in reaction mixtures to *p*-hydroquinone and catechol, respectively. *p*-Benzoquinone, *p*-hydroquinone, and catechol were identified in an experiment in which the reaction mixture was analyzed by VPC without employing sodium sulfite or any other reducing agent in the workup.
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(14) A second-order plot of $[phenol]^{-1}$ vs. time indicates that the reaction is second order overall. The fact that the rate was first order in each reactant was established by initial rate studies which indicated that the rate depended on both phenol and peracetic acid.
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