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Oxidative Coupling Reaction of Phenols with Dichromate

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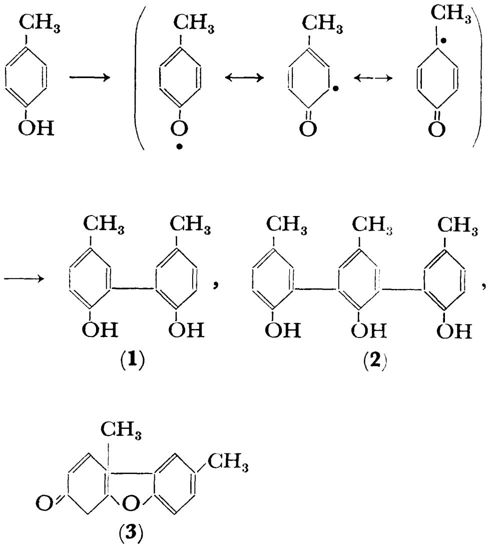
On treatment in an aqueous solution with dichromate, *p*-cresol and creosol readily undergo nuclear oxidative coupling. The yields of dimeric and trimeric cresols and of dimeric ketone are of the same order as the yields of the previously-recorded preparations by one-electron-transfer oxidants. When manganese sulfate is added, these yields are tripled. The probable mechanism of the coupling reaction of phenols with dichromate is discussed.

During the course of an investigation of the mechanism for the gelling reaction of lignin with dichromate,[1,2] it became desirable to examine the coupling reaction of phenols with dichromate.

It has been well known that phenols react with one-electron-transfer oxidants, *e.g.*, persulfate, alkaline ferricyanide or Fenton's reagent, to produce phenoxy-radicals, which then give dimeric or trimeric products by coupling reaction.[3] This oxidation mechanism has been confirmed by the identification of the oxidation products, by the detection of an intermediate phenoxy radical by the ESR technique, and so on. However, the great majority of works on the oxidation of phenols with dichromate have dealt with the preparation of quinone[4]; the only example concerning coupling products was recorded in the case of highly alkylated phenols in 50% acetic acid and 20% sulfuric acid at 50—55°C.[5] Accordingly, it has not yet been established whether the oxidative coupling readily occurs by means of the reaction between phenols and dichromate in an aqueous solution. The present investigation was, therefore, undertaken in order to clarify this problem. In addition, the catalytic effect of the manganese ion upon this reaction will be discussed.

Results and Discussion

The oxidation of phenols by one-electron-transfer oxidants has been reported by a number of workers. In all cases, the initial step has been described as the removal of hydrogen from the phenols by a radical or multivalent metal ion; the further coupling reaction of the resulting aryloxy-radical has also been discussed. For example, the coupling reaction scheme for *p*-cresol is as follows:



In the present experiments, on treatment with the aqueous dichromate, *p*-cresol gave a crystalline fraction (15%) consisting of *ortho*-linked dimeric (**1**) and trimeric (**2**) cresols and the dimeric ketone (**3**) (Table 1); on the other hand, creosol furnished only *ortho*-linked dimeric creosol (7—9%) as a crystalline product (Table 2). Homocatechol, meanwhile, yielded only resinous products. When manganese sulfate was added as a catalyst, the yields of crystalline products from *p*-cresol or creosol were tripled. The total yields of the oxidation products from *p*-cresol were 1.5 times as much as the best yields among the previously-recorded

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[3] W. A. Waters, "Progress in Organic Chemistry," Vol. 5, ed. by J. W. Cook and W. Carruthers, Butterworths, London (1961), p. 1.

[4] J. Cason, "Organic Reaction," Vol. 4, ed. by R. Adams, John Miller & Sons. Inc., New York (1948), p. 305.

[5] H. E. Albert, *J. Amer. Chem. Soc.*, **76**, 4983 (1954).

Table 1. Dichromate oxidation products of *p*-cresol

MnSO$_4$	Total prods. (ppt.) (%)	Ether-insol. prods. (%)	Ether-sol. prods.					Total coupling prods. of (1), (2) and (3) (%)
			Neutral prods.		Alkali-sol. prods.			
			Total crude (%)	Ketone (3) (%)	Total crude (%)	Dimer (1) (%)	Trimer (2) (%)	
None	66	19	20	12	27	2	1	15
8.0 g/*l* (0.053 mol)	74	5	27	17	43	8	6	31
80.0 g/*l* (0.53 mol)	82	2	33	21	47	13	7	41

Table 2. Dichromate oxidation products of creosol

MnSO$_4$	$K_2Cr_2O_7$ mol/*l*	Total prods. (ppt.) (%)	Ether-insol. prods. (%)	Ether-sol. prods.	
				Total crude (%)	Dimer (%)
None	0.047	53	17	36	9.0
None	0.012	58	15	43	7.2
80.0 g/*l* (0.53 mol)	0.012	71	9	62	22.5

preparations;[6-13] in other words, half of the starting material was recovered as crystalline oligomers (Table 3).

When larger quantities of dichromate were employed in the oxidation of creosol, greater quantities of the dimer were obtained. In considering the reaction mechanism described below, this result seems to be due to the fact that comparatively more hexavalent chromium exists than tetra- and pentavalent species. An analysis of the residual resinous products showed that demethylation and further oxygenation occurred.

On the dichromate oxidation of homocatechol, unlike the cases of *p*-cresol and creosol, a major part of the precipitate (60%) was an ether-insoluble fraction; this was an alcohol-soluble complicated resin possibly oxygenated. Also precipitates were traces of unidentified polyphenols and carboxylic acid, detected by the paper chromatography of the ether-soluble fraction. It may be thought that the crystalline oligomer is not obtained, for the resulting products are further oxidized, too.

As is shown in Fig. 1, the velocity of the oxidation reaction increases in the following order: homocatechol>creosol>*p*-cresol. This order is proportional to the electron density of the phenolic hydroxyl group. It seems probable that the initial step in these reactions is an abstraction of one electron. Furthermore, it was detected that the addition of

Table 3. Oxidation products of *p*-cresol weth various oxidants

Oxidants	Dimer (**1**) (%)	Trimer (**2**) (%)	Ketone (**3**) (%)	Total of **1**, **2** and **3** (%)	Ref.
$K_2Cr_2O_7$	2	1	12	15	This pap.
$K_2Cr_2O_7+MnSO_4$ (8 g/*l*)	8	6	17	31	This pap.
$K_2Cr_2O_7+MnSO_4$ (80 g/*l*)	13	7	21	41	This pap.
$Na_2S_2O_8+Ag^+$, Fe^{2+}, Fe^{3+}	7	7	15	29	6
Electrolytic oxidn.	11	7		18	7
Alkaline $K_3Fe(CN)_6$	1 2	2	13	16 17	8
H_2O_2+Peroxidase	2	7	13	22	9
$H_2O_2+Fe^{2+}$	6		4	10	10
Solid $FeCl_3$	10 11	6 9		16 20	11
Aq. $FeCl_3$	5		1	6	11
Cl_2 or $SO_2Cl_2+ZnCl_2$	12 16	3 8		15 24	12
Nickel peroxide	small	small	small	small	13

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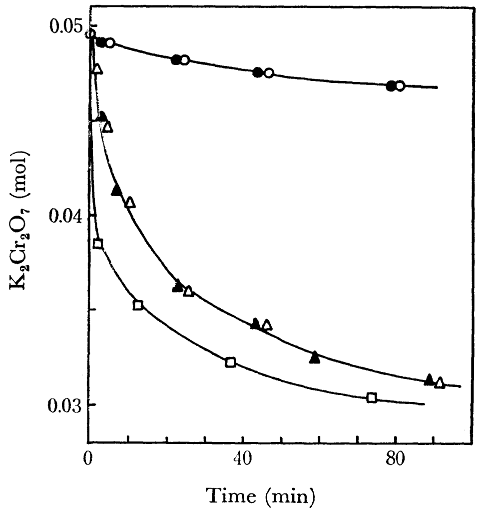

Fig. 1. Dichromate concentration-time curves for oxidation reaction of various phenols.
○●, *p*-cresol; △▲, creosol; □, homocatechol substrates: 0.05 mol, CH_3COOH: 0.2 mol $MnSO_4$; ●▲, 0.5 mol; ○△□, none, 25°C

the manganese ion is independent of the velocity change.

The catalytic effect of the manganese ion in chromium oxidation is of peculiar interest. This effect has been described in the case of alcohols,[14] but not in that of phenols. It is known that divalent manganese (Mn^{2+}) is oxidized to trivalent species (Mn^{3+}) with tetra- and pentavalent chromiums, but not with hexavalent species.[15] It is also known that trivalent manganese reacts with phenols to produce a phenoxy radical, which in turn affords a high yield of oxidative coupling products.[16] As Tables 1 and 2 show the yields of the coupling products of phenols with dichromate about triple when a large amount of the manganese ion is added.

From these facts, when the manganese ion is not present, it may be thought that one mole of chromic acid (CrO_4^{2-}) acts as one equivalent to produce the phenoxy radical; that is, only hexavalent chromium may be effective in producing the phenoxy radical, as is shown in Eq. (1), while the tetra- and pentavalent species may be ineffective. On the other hand, in the case of the presence of a large amount of the manganese ion, one mole of chromic acid has the ability of three equivalents because the trivalent manganese ion, which is produced by the reaction between the divalent manganese ion and penta- or tetravalent chromium, may also be effective in producing the phenoxy radical, as is shown in Eqs. (3) and (4). In conclusion, the mechanism for the coupling reaction of phenols with dichromate in the presence of manganese sulfate may be proposed to be as follows:

$$\text{PhOH} + \text{Cr(VI)} \longrightarrow \text{PhO}\bullet + \text{Cr(V)} \qquad (1)$$

$$\text{PhOH or PhO}\bullet + \text{Cr(V) or Cr(IV)} \longrightarrow \text{Complicated products} \qquad (2)$$

$$\text{Mn}^{2+} + \text{Cr(V) or Cr(IV)} \longrightarrow \text{Mn}^{3+} + \text{Cr(IV) or Cr(III)} \qquad (3)$$

$$\text{PhOH} + \text{Mn}^{3+} \longrightarrow \text{PhO}\bullet + \text{Mn}^{2+} \qquad (4)$$

$$\text{PhO}\bullet + \text{PhO}\bullet \longrightarrow \text{Dimer} \longrightarrow \text{Trimer} \qquad (5)$$

In the absence of manganese sulfate, the reaction mechanism may be expressed by Eqs. (1), (2) and (5).

Experimental

Materials and Procedure. The phenols employed in this study were *p*-cresol, creosol, and homocatechol. The phenols and other reagents were of an analytical reagent grade. The oxidation reactions of the phenols with dichromate were carried out in an aqueous solution containing 1.2% acetic acid under gentle stirring, at a constant temperature, and in air. The consumption of dichromate was measured by the iodometry method.

In these oxidations, turbidity appeared within a few minutes after mixing; the product was eventually isolated quantitatively as a precipitate from a brown solution. In order to remove a small amount of inorganic substances, the product was treated with ether. The ether-soluble product was then separated, by 2N sodium hydroxide, into a neutral fraction and an alkali-soluble polyphenol fraction. The oxidation products were identified by a comparison of their melting points and of the results of elemental analyses of them and their derivatives with those of authentic samples. The melting points were measured with Yanagimoto's micromelting-point apparatus, while the elemental analyses were performed in the Analytical Center of Kyushu University.

Oxidation of *p*-Cresol. *(a) Products of Non-catalyzed Oxidation.* An aqueous solution (1 *l*) containing *p*-cresol (10.8 g, 0.1 mol), potassium dichromate (15 g, 0.05 mol), and acetic acid (12 g, 0.2 mol) was allowed to stand for 92 hr at 25°C. The dry weight of the precipitate was 6.3 g (66% of the weight of the oxidation products), of which the ether-insoluble and alcohol-soluble portion; an amorphous brown powder, composed 1.8 g (19%). The ether-soluble fraction gave a pale yellow, crystalline, neutral material (1.9 g, 20%) and a brown, resinous, alkali-soluble polycresol (2.5 g, 26%). The ether extraction of the aqueous filtrate from the oxidation products yielded a trace of an oily material and unchanged *p*-cresol (1.2 g, 13%).

After crystallization from methanol, the neutral fraction yielded Pummerer's ketone as colorless leaflets (1.1 g, 12%); mp 123.5°C (lit,[6-12] mp 122—128°C) (Found: C, 77.90; H, 6.57%). The alkali-soluble polycresols were distilled *in vacuo* to yield two resinous fractions, (A) (bp 150—190°C/1 mmHg; 0.4 g, 4%) and

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(B) (bp 210—260°C/1 mmHg; 0.5 g, 5%). The fraction (A) was crystallized from benzene to give 2,2′-dihydroxy-5,5′-dimethyldiphenyl (0.2 g, 2%) as colorless prisms; mp 154—155°C (lit,[6] 153—154°C) (Found: C, 78.03; H, 6.47%). This was characterized as the diacetate; mp 87.5°C (lit,[6] 87—88°C) (Found: C, 72.37; H, 6.14%). When the (A) fraction was treated with bromine (2 molar equiv. per mol) in glacial acetic acid, 3,3′-dibromo-2,2′-dihydroxy-5,5′-dimethyldiphenyl was obtained as colorless prisms, mp 141—142°C (lit,[6] 141—142°C) after recrystallization from aqueous ethanol.

The fraction (B), crystallized from benzene, gave colorless 2,2′,2″-trihydroxy-5,5′,5″-trimethyl-*m*-terphenyl (0.1 g, 1%); mp 196.5—197°C (lit,[6] 194—197°C) (Found: C, 78.62; H, 6.16%). When the fraction (B) was treated at room temperature with bromine (2 molar equiv. per mol) in glacial acetic acid, 3,3′-dibromo-2,2′,2″-trihydroxy-5,5′,5″-trimethyl-*m*-terphenyl was obtained; mp 286—288°C (lit,[6] 284—286°C) (Found: C, 52.76; H, 3.95%).

(b) Oxidation Products Catalyzed with Manganese Ion. A mixture like that in (*a*) was stirred for 92 hr at 25°C with manganese sulfate (0.053 or 0.53 mol respectively). Fractionation and the identification of the oxidation products were performed as above. The results are summarized in Table 1.

Oxidation of Creosol. *(a) Products of Non-catalyzed Oxidation.* The following is a typical preparation carried out on a 0.036 molar scale at 25°C. An aqueous solution (1 *l*) containing creosol (5.0 g, 0.036 mol; insoluble above this value), potassium dichromate (3.6 g, 0.012 mol), and glacial acetic acid (12 g, 0.2 mol) was allowed to stand for 20 hr. The dry weight of the precipitate was 2.84 g (57%), of which the ether-insoluble, amorphous brown powder was 0.74 g (15%). The ether-soluble products were distilled *in vacuo* to yield a resinous material; bp 180—260°C/0.7 mmHg (1.1 g, 22%). This fraction was crystallized from benzene to give 2,2′-dihydroxy-3,3′-dimethoxy-5,5′-dimethyldiphenyl (0.36 g, 7.2%) as colorless needles; mp 130.5—131°C (lit,[17] 130°C) (Found: C, 70.65; H, 6.62%). The diacetate, after recrystallization from alcohol, had a mp of 163°C (lit,[17] 162—163°C) (Found: C, 67.18; H, 6.21%). The oily material other than the above crystalline material had a methoxyl content of 19.9%. The ether-insoluble fraction (soluble in alcohol) did not melt below 300°C, and its methoxyl content was 15.8%, which was less than that of the starting material (22.6%). (Found, after correction for inorganic materials: C, 63.35; H, 5.55%. Calcd for creosol; $C_8H_{10}O_2$: C, 69.54; H, 7.29%). When the proportion of dichromate was higher than in the above experiment, the yield of dimer increased from 7.2% to 9.0% (Table 2).

(b) Oxidation Products Catalyzed with Manganese Ion. A mixture like that in (*a*) was stirred for 20 hr at 25°C with manganese sulfate (0.53 mol). The fractionation and identification of oxidation products were performed by the same method as above. The results are summarized in Table 2.

Oxidation of Homocatechol. An aqueous solution (1 *l*) containing homocatechol (4.5 g, 0.036 mol), potassium dichromate (3.6 g, 0.012 mol), and glacial acetic acid (12 g, 0.2 mol) underwent rapid oxidation at 25°C. A rapid darkening and deposit of particles of a brown, amorphous solid occurred. However, the mixture was left for 5 hr. The crude product (2.7 g, 60% of the weight of homocatechol) yielded a large amount of an ether-insoluble fraction as a brown powder which was thought to be polyphenol. The ether-insoluble fraction, subjected to paper chromatography, appeared to consist of alkali-soluble polyphenols and a small amount of carboxylic acid.

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