

Oxidation Studies. Part I. Metal-catalysed Persulphate Oxidation of Some Simple Phenols.

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The oxidation of phenol and *o*-, *m*-, and *p*-cresol by aqueous persulphate solutions is strongly catalysed by silver, ferrous, or ferric, but not by other ions examined. Oxidation by $S_2O_8^{2-}-Fe^{3+}$ is much faster than by Fe^{3+} alone. Reaction is believed to proceed by mechanisms which involve $\cdot SO_4^-$ radicals and, in the case of silver catalysis, transient higher-valency ions, Ag_2^+ or Ag^{3+} .

Resinous polyphenols constitute almost the entire product from phenol and *o*- or *m*-cresol, but with *p*-cresol the following known crystalline products of oxidative coupling ($\sim 30\%$ in all) were isolated: 2 : 2'-dihydroxy-5 : 5'-dimethyldiphenyl, 2 : 2' : 2''-trihydroxy-5 : 5' : 5''-trimethyl-*m*-terphenyl, and a tetrahydrodimethyloxodibenzofuran. In the polyphenols the presence of 3—7 phenol units per molecule is indicated, and they contain, on average, about 0.2 atom of additional oxygen per phenol unit, probably introduced *via* nuclear hydroxylation, since small amounts of surviving mononuclear quinones were detected.

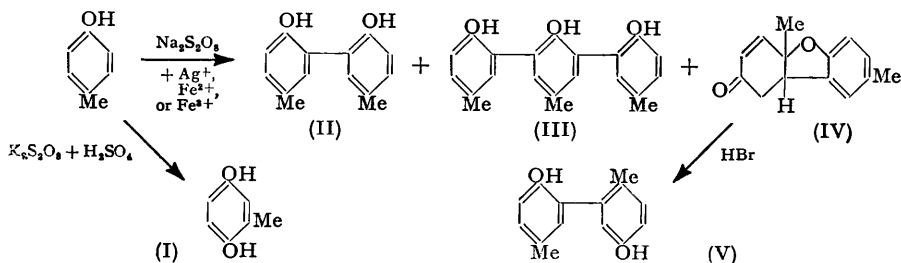
WE recently summarised the results obtained by oxidising various kinds of aromatic compounds with aqueous persulphate solutions, particularly in the presence of metal salts as catalysts (Bacon, Bott, Doggart, Grime, and Munro, *Chem. and Ind.*, 1953, 897). The present communication describes the oxidation, by this method, of phenol and of *o*-, *m*-, and *p*-cresol.

We have found that the inclusion of silver ions, in particular, converts an aqueous persulphate solution into a potent and widely applicable oxidant for organic compounds. This catalytic activity of silver with persulphate, discovered by Marshall (*Proc. Roy. Soc. Edinburgh*, 1891, **18**, 63; 1900, **23**, 163; 1902, **24**, 88), has been applied to inorganic oxidations (*e.g.*, Yost *et al.*, *J. Amer. Chem. Soc.*, 1926, **48**, 152; 1931, **53**, 3349; 1937, **59**, 2129) and to some organic reactions. The latter include the oxidation of oxalic acid (Kempf, *Ber.*, 1905, **38**, 3963; King, *J. Amer. Chem. Soc.*, 1927, **49**, 2689; 1928, **50**, 2089; Allen, *ibid.*, 1951, **73**, 3589), of *p*-benzoquinone (Kempf, *Ber.*, 1906, **39**, 3715), of toluene and thymol (Austin, *J.*, 1911, **99**, 262), of acetone (Bekier and Kijowski, *Roczn. Chem.*, 1935, **15**, 136) and of glycols (Greenspan, *Diss. Abs.*, 1952, **12**, 132). We find, incidentally, that oxidation of acetone is not fast enough to prevent use of aqueous acetone, if desired, as a solvent for some catalysed oxidations (see Table 4).

Crystalline Products from Catalysed Oxidation of the Phenols.—Kumagai and Wolffenstein (*Ber.*, 1908, **41**, 297) reported that acidic aqueous potassium persulphate converts *p*-cresol, at 70—80°, into toluquinol (I), the reaction apparently involving migration of a methyl group (*cf.* Raper, *J.*, 1938, 125). We have confirmed this transformation (unreported experiments by R. Grime) but have found that resins ($\sim 95\%$) greatly predominate over crystalline products. Likewise, oxidation by aqueous sodium persulphate at 20—40° gives resins. At these temperatures reaction is slow ($\sim 0.2\%$ per hr. at 40°; see Table 3) but addition of silver nitrate both catalyses the oxidation and provides a much cleaner, semi-crystalline product (Tables 3 and 4). With $S_2O_8^{2-}$ and Ag^+ in the ratio 10 : 1 the increase in rate of product-formation is of the order of 100-fold and it is still very large with much lower proportions of silver (*e.g.*, at 100 : 1). Of numerous other metal ions tested, only iron salts proved obvious catalysts; both the ferrous and the ferric form were effective and they were comparable in their activity with silver.

Three known, crystalline dehydro-derivatives of *p*-cresol were isolated from the products of catalysed oxidation. The mainly crystalline neutral fraction (20—40% in various runs) yielded a tetrahydrodimethyloxodibenzofuran (IV) and the mainly resinous alkali-soluble polycresol fraction yielded small amounts of 2 : 2'-dihydroxy-5 : 5'-dimethyldiphenyl (II) and 2 : 2' : 2''-trihydroxy-5 : 5' : 5''-trimethyl-*m*-terphenyl (III). The yields of these

three compounds are of the same order as in the best of previously recorded preparations (Table 1). The products were characterised by known derivatives and by the conversion of (II) and (III) into dibromides; ring-opening of (IV) yielded the diphenol (V).



Oxidation of phenol, *o*-cresol, and *m*-cresol was catalysed by silver ions as was that of *p*-cresol, but the precipitated products were entirely resinous and alkali-soluble. In the aqueous phase 1—2% of quinones were detected. As simple quinones readily undergo further oxidation, it is probable that larger amounts were initially formed; from 2:6-xylene-1-ol, which is blocked in both *ortho*-positions, the corresponding quinone is formed in substantial quantities under our conditions (Bacon and Munro, unpublished work).

TABLE 1.

Ref.	Agent	Dimeric phenol (II) (%)	Trimeric phenol (III) (%)	Ketone (IV) (%)
This paper	$\text{Na}_2\text{S}_2\text{O}_8 + \text{Ag}^+, \text{Fe}^{2+}, \text{or Fe}^{3+}$	7	7	15
<i>a</i>	Electrolytic oxidn.	11 (crude)	7 (crude)	—
<i>b</i>	Alkaline $\text{K}_3\text{Fe}(\text{CN})_6$	1—2	2	13
<i>c</i>	$\text{H}_2\text{O}_2 + \text{peroxidase}$	2	7	13
<i>d</i>	$\text{H}_2\text{O}_2 + \text{FeSO}_4$	6	—	4
<i>e</i>	Solid FeCl_3	10—11	6—9	—
<i>e</i>	Aq. FeCl_3	5	—	1
<i>f</i>	$\text{Cl}_2 \text{ or } \text{SO}_2\text{Cl}_2 + \text{ZnCl}_2$	12—16	3—8	—

^a Fichter and Ackermann, *Helv. Chim. Acta*, 1919, 2, 583, who describe (III) as an ether. ^b Pummerer, Melamed, and Puttfarcken, *Ber.*, 1922, 55, 3116; Pummerer, Puttfarcken, and Schopflocker, *ibid.*, 1925, 58, 1808. ^c Westerfeld and Lowe, *J. Biol. Chem.*, 1942, 145, 463. ^d Cosgrove and Waters, *J.*, 1951, 1726, whose yields % are based on non-recovered cresol. ^e Bowden and Reece, *J.*, 1950, 2249. ^f *Idem*, *J.*, 1950, 1686.

Polymeric Products.—The polyphenols which constitute the main products are alkali-soluble resins, and appear to be mainly constituted of three or more phenol units per molecule. They are not the result solely of oxidative coupling, since representative samples (Table 2) contained additional oxygen.

TABLE 2.

	Average no. of phenol nuclei per mole	Average no. of O atoms per phenol nucleus
(<i>a</i>) Ether-insol. polymer from phenol.....	7	1.4
(<i>b</i>) Fraction from chromatography of polyphenol ...	4	1.25
(<i>c</i>) Fraction from chromatography of poly- <i>o</i> -cresol ...	3.5	1.15
(<i>d</i>) Fraction from chromatography of poly- <i>m</i> -cresol	3	1.2

Notes : (i) A product such as (*b*) involves consumption of 1 mole of $\text{Na}_2\text{S}_2\text{O}_8$ per mole of phenol (as actually employed). (ii) In the Experimental section the oxygen is arbitrarily represented as hydroxylic.

Two observations demonstrate the stepwise formation of these complex oxidation products : in oxidation of *p*-cresol the consumption of persulphate continued after precipitation was complete (Table 3); and the crystalline diphenol (V) gradually resinified when stirred with the oxidant. The presence of small amounts of surviving mononuclear quinones in the aqueous phase suggests that extra oxygen may be acquired by introduction of nuclear hydroxyl groups, which then undergo further changes. Apart from this complication, there are two obvious causes of heterogeneity in the polymers. First, the linkages

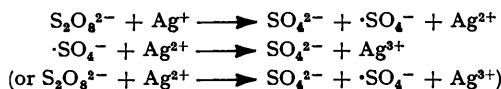
between phenol units may be internuclear, as in (II) and (III), or may be through ether oxygen, as in (IV) (cf. Pummerer *et al.*, *loc. cit.*; *Chem. Ber.*, 1952, **85**, 535; 1953, **86**, 412), or may involve the methyl groups. Secondly, as in the case of phenol-formaldehyde resin formation, the number of structural isomers may vary from a maximum in phenol (which gave the most complex products) to a minimum in *p*-cresol (which gave the simplest products).

Reaction Mechanism.—The primary stage in catalysis of persulphate reactions by ferrous ions is generally accepted as being :



(Merz and Waters, *Discuss. Faraday Soc.*, 1947, **2**, 179; *J.*, 1949, S 15; Kolthoff, Medalia, and Raaen, *J. Amer. Chem. Soc.*, 1951, **73**, 1733; Fordham and Williams, *ibid.*, p. 4855). Phenol oxidation may then involve dehydrogenation ($\text{RH} + \cdot\text{SO}_4^- \longrightarrow \text{R}\cdot + \text{SO}_4^{2-}$), followed by coupling of the resulting radicals (hydroxyaryl or aryloxy) as suggested in the similar case of oxidation by the H_2O_2 - Fe^{2+} system (Cosgrove and Waters, *loc. cit.*).

By analogy, the primary steps in silver catalysis may be represented :



Transient bi- or ter-valent silver ions were postulated in $\text{S}_2\text{O}_8^{2-}$ - Ag^+ systems by Marshall, by Austin, and by Yost (*loc. cit.*) and there is evidence for their existence from other sources (Kleinberg, "Unfamiliar Oxidation States and Their Stabilisation," Univ. Kansas Press, Lawrence, U.S.A., 1950). The production of free radicals in the $\text{S}_2\text{O}_8^{2-}$ - Ag^+ system is supported by the fact that it behaves as a powerful redox catalyst for vinyl polymerisations (Bacon, *Trans. Faraday Soc.*, 1946, **42**, 140; Morgan, *ibid.*, p. 169). Although persulphate and silver salts react rapidly (giving a black hydrolysis product of the higher-valency salt if no oxidisable substance is present), the catalysed phenol oxidations proceed to completion without any special precautions as to the method of mixing the reagents. This suggests that one reaction occurring in the system is a direct oxidation of the phenol by the unstable higher-valency ions, Ag^+ thereby being regenerated (cf. Yost, *loc. cit.*). In the case of iron, this direct oxidation is, of course, observable by employing the ferric salt alone (cf. Bowden and Reece, *loc. cit.*) and it may explain why, here too, mixing conditions are not critical, and why both ferrous and ferric ions are catalysts. It is noteworthy, however, that the iron-catalysed reaction is much faster (yield of product being about ten times as great) as in a comparable reaction in which a ferric salt alone is the oxidant.

EXPERIMENTAL

M. p.s are corrected. Some analyses are by Mr. J. Henry, Microchemical Laboratory, Queen's University, Belfast.

Materials and Procedure.—Sodium persulphate (cf. Table 4) was 97–99% pure. Redistilled laboratory-grade phenols were employed; some comparative experiments were done with *p*-cresol prepared from purified *p*-toluidine. Oxidations were conducted by mixing separate solutions of the phenol, persulphate, and catalyst, and gently stirring the mixture, at constant temperature, in air.

In catalysed oxidations, turbidity developed within a few minutes of mixing, and the product was eventually recovered quantitatively as a precipitate from a brown solution. When treated with ether, the dried product left some insoluble residue, usually small and contaminated with inorganic material. The ether-soluble product was separated, by 2*N*-sodium hydroxide, into a neutral fraction and an alkali-soluble polyphenol fraction.

Oxidation of p-Cresol.—(a) *Products of silver-catalysed oxidation.* The following is typical of preparations carried out on a 0.1–1.5 molar scale at room temperature. An aqueous solution (1 l.) containing pure synthetic *p*-cresol (10.8 g., 0.1 mole), sodium persulphate (0.1 mole), and silver nitrate (0.01 mole) was left for 24 hr. at 17°. The dry weight of the precipitate was 10.5 g., of which the ether-insoluble portion, an amorphous brown powder, was 0.22 g. Treatment of the ether-soluble product gave a pale yellow, crystalline, neutral fraction (2.8 g., 26%) and a

brown, resinous, alkali-soluble polycresol fraction (7.8 g., 72%). Ether-extraction of the aqueous filtrate from the oxidation products yielded only a trace of oily material.

After one crystallisation from methanol the neutral fraction yielded tetrahydrodimethyloxodibenzofuran (IV) as colourless leaflets (1.65 g., 15%), m. p. 123.5°, raised to 125—125.5° by sublimation at 0.1 mm.; m. p.s. previously recorded (Table 1) vary from 122° to 128° (Found : C, 78.4; H, 6.5. Calc. for $C_{14}H_{14}O_2$: C, 78.5; H, 6.5%). The oxime had m. p. 199—201° (decomp.) (Found : C, 73.1; H, 6.5; N, 5.9. Calc. for $C_{14}H_{15}O_2N$: C, 73.4; H, 6.5; N, 6.1%); Pummerer *et al.* (*loc. cit.*) give 203—204°, Westerfeld and Lowe (*loc. cit.*) give 198—200°, and Bowden and Reece (*loc. cit.*) give 195°. The semicarbazone had m. p. 259° (decomp.); Pummerer *et al.* give 249—250° (decomp.) and Westerfeld and Lowe give 255—256°.

Some unchanged *p*-cresol (0.75 g., 7%) was removed from the alkali-soluble fraction by steam-distillation. The residual polycresols were distilled *in vacuo* to yield resinous fractions (A), b. p. 140—160°/1 mm. (1.48 g., 13% of the wt. of *p*-cresol), and (B), b. p. 220—280°/1 mm. (2.75 g., 25%). Fraction (A) crystallised from benzene, to give 2 : 2'-dihydroxy-5 : 5'-dimethyldiphenyl (II) (0.8 g., 7%) as colourless prisms, m. p. 153—154° (Found : C, 78.5; H, 6.3. Calc. for $C_{14}H_{14}O_2$: C, 78.5; H, 6.5%), characterised as the diacetate, m. p. 87—88° (cf. Pummerer *et al.*, *loc. cit.*), and by treatment with bromine (2 molar equiv. per mole) in glacial acetic acid, (? 3 : 3'-dibromo-2 : 2'-dihydroxy-5 : 5'-dimethyldiphenyl being obtained in colourless needles, m. p. 141—142°, after recrystallisation from aqueous ethanol (Found : C, 45.6; H, 3.0; Br, 42.8. $C_{14}H_{12}O_2Br_2$ requires C, 45.2; H, 3.3; Br, 42.9%).

Fraction (B), crystallised from benzene, gave colourless 2 : 2' : 2''-trihydroxy-5 : 5' : 5''-trimethyl-*m*-terphenyl (III) (0.75 g., 7%), m. p. 194—196° (Found : C, 78.6; H, 6.45. Calc. for $C_{21}H_{20}O_3$: C, 78.7; H, 6.3%); Pummerer *et al.* (*loc. cit.*) give m. p. 194°, Westerfeld and Lowe (*loc. cit.*) give 196.5°, and Bowden and Reece (*loc. cit.*) give 197°. Treatment, at room temperature, with bromine (> 2 mol.) in glacial acetic acid yielded a crude derivative (99%, calc. as dibromide), which, after two recrystallisations from ethanol, had m. p. 284—286° (decomp.). Analysis (except that the bromine value is a little high) indicated the expected dibromide, (? 3 : 3'-dibromo-2 : 2' : 2''-trihydroxy-5 : 5' : 5''-trimethyl-*m*-terphenyl (Found : C, 52.9; H, 3.9; Br, 34.6. $C_{21}H_{18}O_3Br_2$ requires C, 52.7; H, 3.8; Br, 33.5%).

Alternatively, the crude polycresols were separated chromatographically on alumina (Peter Spence, Type H), with chloroform and ethanol, total recoveries being 60—90%. The first fraction was (unexpectedly) tetrahydrodimethyloxodibenzofuran (2% of the polycresol sample), m. p. and mixed m. p. 123.5—124.5° (semicarbazone, m. p. 261—262°), followed by resinous fractions (nearly 50% of the sample) and then by semi-crystalline fractions (about 40% of the sample). The semi-crystalline products were recrystallised to give, from successive fractions, the phenols (II) and (III) (about 5% each, on *p*-cresol).

(b) *Rates of catalysed and non-catalysed oxidations.* Precipitated reaction products (from 250 ml.; solutions left for varying times) were isolated on tared crucibles. The amount of persulphate which had decomposed was determined by titration of the acid present in the filtrates. Yields (Table 3) are expressed as % by wt. of *p*-cresol.

TABLE 3.

	<i>p</i> -Cresol, 0.1M Na ₂ S ₂ O ₈ , 0.1M AgNO ₃ , 0.01M 20°				<i>p</i> -Cresol, 0.1M Na ₂ S ₂ O ₈ , 0.1M AgNO ₃ , 0.01M 40°					<i>p</i> -Cresol, 0.1M Na ₂ S ₂ O ₈ , 0.1M 40°			
	3	8	17	25	1.2	2.1	3.0	5.5	19	20	49	100	193
Time (hr.)	3	8	17	25	1.2	2.1	3.0	5.5	19	20	49	100	193
Persulphate consumed (%)	33	60	88	95	52	72	86	95	98	21	39	63	90
Total product (%)	52	100	100	100	76	98	99	99	100	7	9	13	33
Ether-insol. product (%)...	0	0	3	2	0	1	2	3	2				
Neutral product (%)	18	40	42	40	29	40	41	38	41				
Polycresols (%)	34	60	55	58	47	57	56	58	57				

(c) *Catalysed oxidations at 40°.* See Table 4.

When a higher proportion of persulphate and a lower proportion of silver were used, at a higher concentration and at a higher temperature (0.125 mole of *p*-cresol, 0.25 mole of Na₂S₂O₈, 0.001 mole of AgNO₃, stirred in 100 ml. of water, at 60° for 2 hr.), 28% of the persulphate was converted into oxygen and the product (100% yield) afforded (i) ether-insoluble resin (16%), corresponding in analysis to (C₇H_{7.6}O_{5.3})_n, (ii) neutral fraction (41%) yielding pure ketone (15%), (iii) polycresol fraction (43%) yielding 2 : 2'-dihydroxy-5 : 5'-dimethyldiphenyl (3%) by distillation at 1 mm.

(d) *Trials of various metal-ions as oxidation catalysts.* Trials were carried out under standard conditions (Table 3), at 40° for 20 hr., purified reagents being used. Silver nitrate, ferrous sulphate, and ferric ammonium sulphate showed effects like those reported in Table 4. The following showed no catalytic effect, *i.e.*, a trace of tar was precipitated and the odour of *p*-cresol persisted: copper nitrate, potassium gold cyanide, zinc sulphate, mercurous nitrate, potassium aluminium sulphate, thallos nitrate, ceric ammonium nitrate, thorium nitrate, stannous or stannic sulphate, lead nitrate, vanadium sulphate (vanadium pentoxide dissolved in concentrated sulphuric acid), bismuth sulphate, chromium potassium sulphate, ammonium molybdate, sodium tungstate, uranyl nitrate, manganese sulphate, cobalt nitrate, and nickel sulphate.

TABLE 4.

1-1. scale; 0.1M-*p*-cresol, 0.1M-persulphate, 0.01M-catalyst; yields as % by wt. of *p*-cresol.

Expt.	Solvent	Per-sulphate	Catalyst	Total time of treatment (hr.)	Total product (%)	Ether-insol. product (%)	Neutral product		
							Total crude (%)	Pure ketone (%)	Poly-cresols (%)
1	H ₂ O	Na ₂ S ₂ O ₈	None	24	10	—	—	—	—
2	"	"	AgNO ₃	13	98	3	34	18	62
3	"	K ₂ S ₂ O ₈	"	17	99	3	19	11	78
4	"	(NH ₄) ₂ S ₂ O ₈	"	19	100	3	19	13	79
5	Aq. acetone (1 : 1 v/v)	Na ₂ S ₂ O ₈	"	90	98	36	17	8	45
6	H ₂ O	"	FeSO ₄	40	98	1	23	9	77
7	"	"	Fe ₂ (SO ₄) ₃	24	96	—	16	8	79

(1) 90% of the cresol was recovered unchanged from the aqueous phase. The product, a resin (*M*, ~250) yielded a little oil and crystals, m. p. 147—150°, on sublimation at 120°/0.05 mm. (4) Gas evolution, 62 ml. at N.T.P., representing 5.5% persulphate decomposition (if oxygen) or 2.8% (if nitrogen). (5) Reaction was almost complete in ~10 hr. (compared with ~5 hr. in water). After 7 days at 20° (precipitation almost complete in ~60 hr.) the neutral fraction was similar, but the ether-insoluble fraction was only 3%. In absence of *p*-cresol, persulphate decomposition at 20° was ~95% in ~50 hr. in both water and 1 : 1 aqueous acetone, whilst at 40° 12 hr. were required in water and 5 hr. in 1 : 1 aqueous acetone. (6) Transient deep blue colour; the course of the reaction and appearance of the products were similar to those observed in silver-catalysis. (7) Ferric ammonium sulphate used. Reaction proceeded similarly to (6).

(e) *Comparison of ferric-catalysed persulphate oxidation with oxidation by ferric salt.* Comparative experiments were carried out for 4 hr. at 40° with aqueous solutions (900 ml.) containing (i) *p*-cresol (0.1 mole) and ferric ammonium sulphate (0.1 mole), and (ii) *p*-cresol (0.1 mole), sodium persulphate (0.05 mole, equivalent in oxidising power to 0.1 mole of ferric salt), and ferric ammonium sulphate (0.005 mole). The former yielded 1.0 g. (9%) of rather oily precipitate and the latter yielded 8.2 g. (76%) of precipitate of the usual type.

(f) *Catalysed persulphate oxidation of 2 : 5'-dihydroxy-2' : 5-dimethyldiphenyl.* Tetrahydrodimethyloxodibenzofuran (IV) (10 g.), prepared as described under (a), was converted by hydrobromic acid into 2 : 5'-dihydroxy-2' : 5-dimethyldiphenyl (V), obtained, after recrystallisation, as a white powder (5.6 g.), m. p. 161—161.5° (Pummerer *et al.*, *loc. cit.*, give 158°; Westerfeld and Lowe, *loc. cit.*, give m. p. 157.5—158.5°). This phenol (5.35 g., 0.025 mole) was stirred for 7 days at 40° in an aqueous solution (250 ml.) of sodium persulphate (0.025 mole) and silver nitrate (0.0025 mole). The filtered and dried product (5.72 g., 107% of the wt. of the phenol) yielded a resinous ether-insoluble fraction (1.87 g., 33%) of high ash-content. The ether-soluble product yielded a trace (0.03 g., 0.5%) of oily neutral material and a resinous alkali-soluble fraction (3.81 g., 67%), which was chromatographed (benzene and ether) on silica gel. The first fractions contained unchanged dihydroxydimethyldiphenyl (0.95 g., 18%), m. p. 159—161°, mixed m. p. 160—161.5°, but the later fractions were entirely resinous.

Oxidation of Phenol.—An aqueous solution (500 ml.) containing phenol (4.70 g., 0.05 mole), sodium persulphate (0.05 mole), and silver nitrate (0.005 mole) underwent rapid oxidation at 40°, but was left for 20 hr. The total crude tarry product (3.81 g., 81% of the wt. of phenol) was repeatedly triturated with ether, which left undissolved about 1.6 g. (34%) of dark resin, soluble in aqueous sodium hydroxide and in acetone, though not in benzene. Analysis corresponded approximately with polyphenols containing an average of 7 benzene nuclei and 10 (?) hydroxyl groups per mole [Found: C, 72.0; H, 4.6%; *M* (Rast), 670. Calc. for C₄₂H₂₀(OH)₁₀: C, 72.6; H, 4.4%; *M*, 694]. The ether-soluble products contained traces of tarry neutral material (0.2%) and unchanged phenol (1%) but were essentially alkali-soluble polyphenols (2.23 g.,

47%), which were chromatographed on alumina, benzene, ether, chloroform, and methanol being used. About half of the material could not thus be removed from the column. All the fractions were resinous. A typical sample corresponded approximately in analysis with polyphenols containing an average of 4 benzene nuclei and 4.5 (?) hydroxyl groups per mole [Found: Ash, 0.9, 2.2, 0; C, on ash-free basis, 75.9, 75.2, 75.6; H, on ash-free basis, 5.1, 5.0, 5.2%; *M* (Rast), 356, 385. Calc. for $C_{24}H_{13.5}(OH)_{4.5}$: C, 76.2; H, 4.8%; *M*, 381].

The red aqueous filtrate from the oxidation products possessed a strong odour of both phenol and *p*-benzoquinone. Ether-extraction yielded red needles (0.87 g., 18.5% of the wt. of phenol taken for oxidation), apparently a mixture of unchanged phenol with the red adduct of phenol and *p*-benzoquinone, but neither this product nor artificial mixtures of phenol and *p*-benzoquinone could be satisfactorily separated into pure components. The quinone content of the mixture was therefore determined by Willstätter and Majima's iodide method (*Ber.*, 1910, 43, 1175). Artificial mixtures of phenol and *p*-benzoquinone gave results within 1% of the theoretical values (recommended time of shaking increased from 3 to 10 min.) and the reaction product was found to contain 7% of *p*-benzoquinone, corresponding with 1% conversion of the original phenol.

Oxidation of o-Cresol.—*o*-Cresol (0.05 mole) was oxidised similarly to phenol. Rapid darkening and deposition of particles of black, amorphous solid occurred. The reaction product (4.85 g., 90% of the wt. of *o*-cresol) contained 0.20 g. (4%) of an ether-insoluble fraction, which was readily soluble in 2*N*-sodium hydroxide and gave an ash-content of 14%. The ether-soluble product consisted of a small neutral fraction (4%), a trace of unchanged *o*-cresol, and the main alkali-soluble polycresol fraction (4.68 g., 87%). The last was separated by chromatographic treatment, as described for phenol products, into 25 resinous fractions (75% recovery from the column), two of which showed the following compositions: (A) Found: Ash, 0.3, 0.6; C, on ash-free basis, 77.4, 77.5; H, on ash-free basis, 6.2, 6.2%; *M* (Rast), 374, 385. (B) Found: ash, nil; C, 77.0, 76.8; H, 6.2, 6.2% [Calc. for polycresols with an average of 3 benzene nuclei and 3.5 (?) hydroxyl groups per mole, $C_{21}H_{16.5}(OH)_{3.5}$: C, 76.8; H, 6.1%; *M*, 328; for polycresols with an average of 4 benzene rings and 4.5 (?) hydroxyl groups per mole, $C_{28}H_{21.5}(OH)_{4.5}$: C, 77.4; H, 6.0%; *M*, 434].

The red-brown aqueous filtrate from the oxidation products yielded, on ether-extraction, a red mixture of crystals and phenolic oil (0.47 g., 9% of the wt. of *o*-cresol). Analysis of this by the method described under phenol indicated a quinone (? toluquinone) content of 20%, corresponding with 2% conversion of the original *o*-cresol.

Oxidation of m-Cresol.—*m*-Cresol (0.05 mole) was oxidised similarly to phenol. Formation of precipitate, consisting of red-brown powder and tar, was rapid. The crude product (5.28 g., 98% of the wt. of cresol) yielded a small ether-insoluble fraction (1%) as a red-brown powder with a high ash-content. The ether-soluble product consisted of alkali-soluble polycresols (5.0 g., 93%), a little unchanged cresol (3%), and neutral material (0.7%). The polycresols, subjected to chromatography, as described for the phenol products, yielded 14 resinous fractions (86% recovery from the column). A sample, representative of the earlier fractions, corresponded approximately in analysis with an average of 3 benzene nuclei and 3.5 (?) hydroxyl groups per mole [Found: C, 76.8, 76.9; H, 6.5, 6.4%; *M* (Rast), 349, 308. Calc. for $C_{21}H_{16.5}(OH)_{3.5}$: C, 76.8; H, 6.1%; *M*, 328].

Ether-extraction of the aqueous filtrate from the oxidation products yielded some phenolic brown oil (0.08 g., 1.5% of the wt. of cresol). Analysis as described under phenol, indicated a quinone (? toluquinone) content of 19%, corresponding with only 0.3% conversion of the cresol.