Macromolecules

Volume 4, Number 4   July–August 1971

Some Studies of Oxidative Coupling of Phenols

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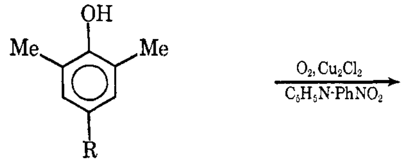
ABSTRACT: The failure of 4-(2′,6′-dimethylphenyl)-2,6-dimethylphenol and 4-phenoxy-2,3,5,6-tetramethylphenol to polymerize by oxidative coupling is in accord with the "quinone ketal" mechanism[2–4] for oxidative coupling but not with the "terminal coupling" mechanism.[5] The oxidative coupling of ID and IE to give polyxylenol (II) is in accord with induced carbonium ion character of the quinone ketal intermediate, as suggested by McNelis.[4] The kinetics of the oxidative coupling reaction are first order in oxygen pressure, first order in copper catalyst concentration, and independent of the phenol concentration, although the rate of phenol oxidation is influenced by substituents on the phenol. These observations are in accord with the hypothesis that the slow, rate-determining step is between oxygen and a copper(I)–phenol complex. Some suggestions are advanced to account for the role of increased amine coordination in shifting the coupling from C–C to C–O.

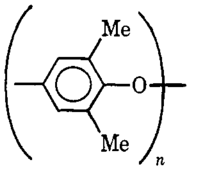
Cooper and coworkers,[2] Mijs and coworkers,[3] and McNelis[4] have advanced evidence and arguments in support of the "quinone ketal" rearrangement or fission mechanisms for oxidative coupling of 2,6-xylenol (I, R = H) to polyxylenol (II) and contrary to the "terminal coupling" mechanism we had advanced earlier.[5]

We report here further studies of this reaction which provide additional strong support for the quinone ketal mechanism and evidence against the terminal coupling mechanism.

We have studied the oxidation of many analogs of 2,6-xylenol, *e.g.*, IA–IG, by oxygen catalyzed by cuprous chloride in pyridine–nitrobenzene and have found that only ID and IE produce polyxylenol.

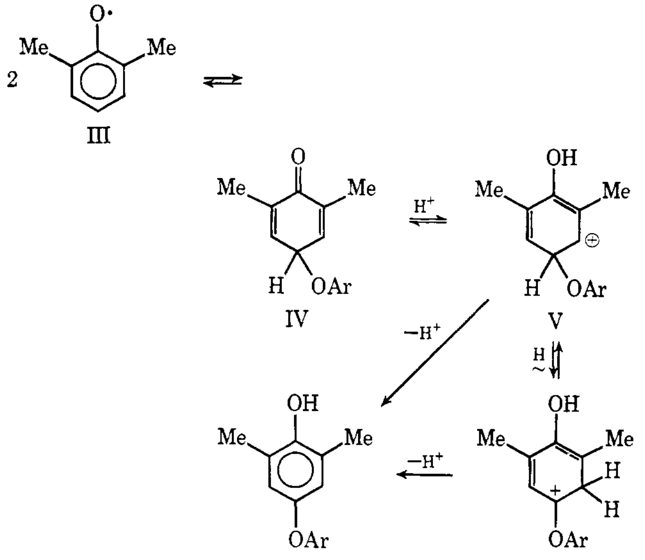


IA, R = Me
B, R = Et
C, R = *i*-Pr
D, R = *tert*-Bu
IE, R = CH_2OH
F, R = OCH_3
G, R = CH_2OEt



II, for R = H, *tert*-Bu, $HOCH_2$

The fact that only the *tert*-butyl and hydroxymethyl groups are eliminated from the 4 position to give polyxylenol offers some support for the mechanism proposed by McNelis[4] for the migration of a proton from the 4 to the 3 position during oxidative coupling.



VII, Ar = 2,6-dimethylphenyl   VI

Coupling of the radicals III to give the keto dimer IV could proceed onward to the dimer phenol VII by either acid- or base-catalyzed enolization. McNelis[4] suggests that acid-catalyzed isomerization would proceed through V, which could either lose a proton directly or isomerize to the cation VI, in which the 3 and 4 protons have become equivalent. This would offer an alternative to the terminal coupling mechanism to explain our tritium labeling experiments[5] which showed that some 4-^{3}H was retained and some 3-^{3}H was lost in polyxylenol formed by oxidative coupling.

Of all the 4 substituents, A–G, we have studied, the two which are lost in oxidative coupling (from ID and IE) to produce polyxylenol are those which would produce the most

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[1] From the doctoral dissertation of Kenji Nakaoka, University of Pennsylvania, 1968, supported in part by General Tire and Rubber Co. and Toyo Rayon Co.

[2] G. D. Cooper, H. S. Blanchard, G. F. Endres, and H. Finkbeiner, *J. Amer. Chem. Soc.*, **87**, 3996 (1965).

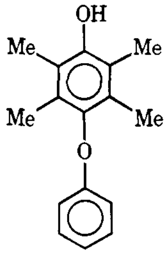
[3] W. J. Mijs, O. E. van Lohuizen, J. Bussink, and L. Vollbracht, *Tetrahedron*, **23**, 2253 (1967).

[4] E. McNelis, *J. Org. Chem.*, **31**, 1255 (1966).

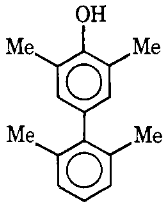
[5] W. A. Butte and C. C. Price, *J. Amer. Chem. Soc.*, **84**, 3567 (1962).

stable cations by elimination from the intermediate corresponding to V. The polymer obtained from ID showed some *tert*-butyl by nmr, perhaps due to end groups and/or to dimer peroxide. The polymer from IE was accompanied by 4-formyl-2,6-xylenol, a product also obtained from IA and IG.

We have also prepared two analogs of the dimeric phenol VII (which is readily converted to polyxylenol), VIII and IX.

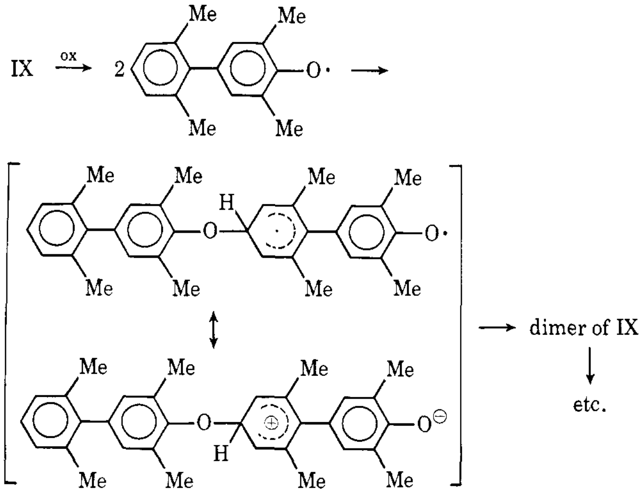


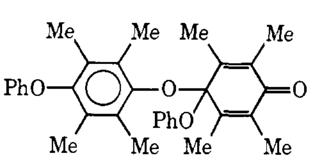
VIII



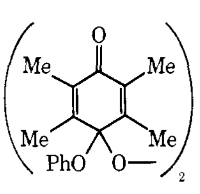
IX

Each of these should be readily convertible to high polymer through the terminal coupling mechanism, illustrated for the case of IX. This "monomer," IX, could not, however, convert to polymer by the quinone ketal mechanism, since the product of C_4–O coupling would not be a ketal. While oxygen (0.33 mmol per millimole of IX) was consumed by IX, the ir and nmr spectra of the oil recovered in 95% yield were nearly identical with those of the starting material. The radical from VIII could give a quinone ketal X by C_4–O coupling, but one with a high degree of steric hindrance.





X



XI

Phenol VIII consumed oxygen (0.8 mmol per millimole of VIII), indicating conversion to radicals, but the product isolated was not polymeric. The peroxide titer and nmr and ir data suggested that it was principally dimeric peroxide XI and its 2,4′ and 2,2′ isomers. These experimental facts are as expected for the quinone ketal mechanism but not the terminal coupling mechanism and thus support the former.

If electron transfer between phenyl groups at a diaryl ether link had been possible,[6] it would have been possible for the 4-bromo derivative of VIII to undergo polymerization by a bromo-displacement mechanism.[7] This possibility was checked by preparing 4′-bromo-VIII and subjecting it to conditions used for polymerization of 4-bromoxylenol.[7] The only identifiable material isolated was starting material in 89% yield.

Table I
Effect of Reaction Volume on Rate of Oxygen Consumption

Volume,[a] ml	mmol of O_2 min^{-1}	mmol of O_2 min^{-1} l.$^{-1}$
30	0.113	3.8
20	0.122	6.1
10	0.0760	7.6
7.5	0.0760	10.1
5.0	0.0685	13.7
3.75	0.0453	12.1
2.5	0.0273	10.9

[a] The amounts of reactants were 22.5 ml of nitrobenzene, 6.75 ml of pyridine, 732 mg of xylenol, and 30 mg of cuprous chloride; P_{O_2}, 1 atm; 25°.

A number of efforts were made to prepare the 4′-bromo derivatives of VII and IX, but without success. VII, its ether, and its acetate ester all brominated preferentially in the 3 position and IX brominated in the 3′ position. It was therefore not possible for us to check the bromo-displacement polymerization on these bromophenols.[8]

We can conclude, from all the tests we have been able to report here, that polymerization mechanisms requiring electron transfer past the diaryl ether oxygen atom have not been successful under any conditions employed. It therefore seems clear that this type of mechanism is not favored for any of the systems so far tested.

Since 4-bromodurenol failed to polymerize under the conditions by which 4-bromo-2,6-xylenol[7] was readily converted to high polymer, and in view of the reluctance of VIII to polymerize, we have studied the oxidative coupling of durenol. It does indeed oxidize and is converted, although in poorer yield than 2,6-xylenol, to a polymeric material. Our product has markedly different properties from those reported by McNelis[9a] but is more like those reported by Huysmans and Waters.[9b] Some of our product melted as high as 345° and was insoluble in common solvents. A more soluble fraction, mp 330°, showed a single proton resonance (at δ 1.99) as expected for polydurenol. This polymer also showed almost no carbonyl stretching (near 1650 cm^{-1}, characteristic of quinone ketals) and no free hydroxyl (3600 cm^{-1}, characteristic of hindered phenols).

Kinetics

A number of factors affecting the rate of oxidative coupling of 2,6-xylenol were studied by measuring the change in oxygen pressure in a closed system at 25°.[10] It was first shown that conditions could be established in which oxygen diffusion was not the rate-controlling process. The data summarized in Table I indicate that, for the reaction vessel and stirring

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(6) D. A. Bolon, *J. Amer. Chem. Soc.*, **88**, 3148 (1966), has shown that for the radical 4-phenoxy-2,6-di-*tert*-butylphenoxy, esr data indicate no such transfer.

(7) G. D. Staffin and C. C. Price, *ibid.*, **82**, 3632 (1960).

(8) S. B. Hamilton, Jr., and H. S. Blanchard, *J. Org. Chem.*, **35**, 3342, 3348 (1970), have recently reported the successful synthesis of 4′-bromo-VII and indicate their intent to study its behavior in oxidative polymerization.

(9) (a) E. McNelis, U. S. Patent 3,220,979; *Chem. Abstr.*, **64**, 6843*f* (1966); (b) W. G. B. Huysmans and W. A. Waters, *J. Chem. Soc. B*, 1163 (1967).

(10) G. F. Endres, A. S. Hay, and J. W. Eustance, *J. Org. Chem.*, **28**, 1300 (1963).

TABLE II
EFFECT OF PYRIDINE CONCENTRATION ON OXYGEN CONSUMPTION[a]

Pyridine, ml	Mole ratio C_5H_5N/Cu_2Cl_2	mmol of O_2 min^{-1}
0	0	0
0.01	0.6	0.008
0.025	1.6	0.067
0.05	3.1	0.128
0.10	6.15	0.147
0.25	15.5	0.163
0.5	30.9	0.161
1.0	61.5	0.149
4.5	278	0.124
15.0[b]	925	0.067

[a] Xylenol, 488 mg; nitrobenzene, 15 ml; Cu_2Cl_2, 20 mg; P_{O_2}, 1 atm; 25°. [b] No nitrobenzene was added in this reaction.

conditions employed, the rate becomes independent of oxygen diffusion at volumes of 5 ml or less. At larger volumes and thus less efficient mixing, it is, however, in part diffusion controlled, a factor perhaps responsible for the earlier statement that the kinetics are "quite complicated."[10]

A feature of the kinetics, as shown below, is that the reaction is pseudo zero order, since it is dependent on oxygen pressure and catalyst concentration (both constants for a given experiment) and independent of xylenol concentration. For example, a sixfold change of xylenol concentration under the conditions of Table I gives rates of oxygen consumption differing by less than 5%, although of course the total amount of oxygen consumed at complete reaction was proportional to the initial xylenol concentration. A plot of oxygen consumed *vs.* time is thus a straight line for most of the course of the reaction, usually with a short induction period. It is thus convenient to record the rates of reaction simply as the rate of oxygen consumption.

It has been shown earlier[10] that the ratio of ligand pyridine to copper is an important factor influencing the rate and course of oxidative coupling of xylenol. Our data on such a study in nitrobenzene are summarized in Table II. They indicate a maximum rate at a ligand-to-copper mole ratio of 15–30. The earlier studies in *o*-dichlorobenzene report a maximum at a ratio of 100.[10]

In Table III, data on the effect of changing catalyst concentration are given, showing that the rate of oxygen consumption is directly proportional to the catalyst concentration at a fixed catalyst-to-pyridine ratio.

Table IV shows data on the change in rate with oxygen pressure. Except for the lowest oxygen pressure employed (where the diffusion rate may become significant), the reaction shows a rate dependent on the first power of oxygen pressure over a threefold pressure range.

TABLE III
EFFECT OF CHANGING CATALYST CONCENTRATION ON RATE OF OXYGEN CONSUMPTION[a]

Cu_2Cl_2, mg	C_5H_5N, ml	mmol of O_2 min^{-1}	mmol of O_2 min^{-1} $Cu_2Cl_2$$^{-1}$
0.312	0.070	0.0050	0.016
0.625	0.140	0.0096	0.015
1.25	0.281	0.0198	0.016
2.50	0.563	0.0343	0.014
5.0	1.125	0.0692	0.014

[a] Xylenol, 122 mg; nitrobenzene, 3.75 ml; P_{O_2}, 1 atm; 25°.

TABLE IV
EFFECT OF OXYGEN PRESSURE ON OXYGEN CONSUMPTION[a]

P_{O_2}, atm	mmol of O_2 min^{-1}	mmol of O_2 min^{-1} $P_{O_2}^{-1}$
0.21	0.009	0.044
0.50	0.030	0.060
0.75	0.047	0.063
1.00	0.068	0.068
1.25	0.077	0.062
1.50	0.087	0.058

[a] Xylenol, 122 mg; nitrobenzene, 3.75 ml; pyridine, 1.125 ml; Cu_2Cl_2, 5 mg; 25°.

Experiments with other copper compounds showed cuprous chloride to be much superior to cupric acetate (15% of Cu_2Cl_2 rate) or cuprous bromide (3% of Cu_2Cl_2 rate). Cuprous cyanide, copper powder, and cupric chloride, bromide, oxide, and carbonate were ineffective as catalysts.[11]

The effects on rate of oxygen consumption of a number of additives and of altering the "inert" solvent from nitrobenzene are shown in Tables V and VI. The autoinhibitory effect of the bromophenols (Table VI) is presumably due to release of hydrogen bromide during polymerization, since this was shown to be a strong inhibitor. While methanol and 2-propanol gave the fastest rates of oxidation, polyxylenol is not soluble in these media, precipitating from solution before conversion to high-molecular-weight polymer was completed.

A large number of analogs of xylenol were oxidized, and the rates of oxygen consumption are summarized in Table VII. These data clearly indicate the importance of electron-donor groups in increasing the rate of oxygen consumption and of electron-withdrawing groups in retarding the rate, although the differences in rate are much smaller than for

TABLE V
EFFECT OF ADDED REAGENTS ON OXYGEN CONSUMPTION

Additive[a]	mmol of O_2 min^{-1}	Additive[a]	mmol of O_2 min^{-1}
None	0.122	4-Bromoxylenol	0.10[b]
CH_3OH	0.135	4-Bromodurenol	0.08[b]
H_2O	0.105	CH_3COOH	0.001
40% CH_2O	0.105	Concd HCl	0
4-Nitroxylenol	0.078	Concd HBr	0

[a] Xylenol, 488 mg; nitrobenzene, 15 ml; pyridine, 4.5 ml; Cu_2Cl_2, 20 mg; P_{O_2}, 1 atm; 25°; additive, 100 mg. [b] Both bromophenols showed the initial rate recorded, but the reactions were autoinhibitory and soon slowed to 0.008 and 0.003 mmol of O_2 min^{-1}, respectively.

TABLE VI
EFFECT OF SOLVENT ON OXYGEN CONSUMPTION

Solvent[a]	mmol of O_2 min^{-1}	Solvent[a]	mmol of O_2 min^{-1}
Methanol	0.225	Nitrobenzene	0.144
2-Propanol	0.225	Chloroform	0.090
DMF	0.190	Benzyl alcohol	0.090
Bromobenzene	0.190	DMSO	0.081
Benzene	0.170		
1,4-Dioxane	0.144	Pyridine	0.045

[a] Xylenol, 244 mg; pyridine, 0.125 ml, Cu_2Cl_2 5 mg; solvent, 3.75 ml; P_{O_2}, 1 atm; 25°.

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(11) See also H. Finkbeiner, A. S. Hay, H. S. Blanchard, and G. F. Endres, *J. Org. Chem.*, **31**, 549 (1966).

Table VII
Rate of Oxygen Consumption for Xylenol Analogs[a]

Phenol[b] 2,6-	Phenol[b] 4-	mmol of O_2 min^{-1}
Me_2	MeO	0.163
Me_2	Me	0.130
Me_2	*i*-Pr	0.121
Me_2	Et	0.108
Me_2	H	0.068
Me_2	H (3,5-Me_2)	0.065
Me_2	*tert*-Bu	0.063[c]
Me_2	$EtOCH_2$	0.061
Me_2	2′,6′-Me_2PhO	0.059
Me_2	PhO (3,5-Me_2)	0.056[c]
Me_2	$HOCH_2$	0.036
H, Me	H	0.013
H, Ph	H	0.007
H_2	Me	0.005
H_2	H	0.004
Me_2	2′,6′-Me_2Ph	0.004
H_2	Ph	0.002

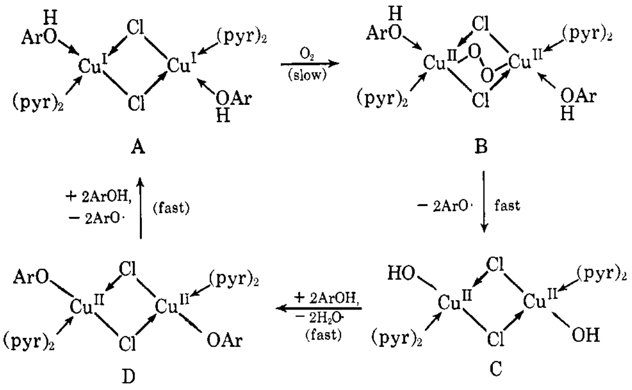
[a] Phenol, 1 mmol; nitrobenzene, 3.75 ml; pyridine, 1.125 ml; Cu_2Cl_2, 5 mg; P_{O_2}, 1 atm; 25°. [b] 4-Formyl-, 4-acetyl-, 4-bromo-, and 4-nitro-2,6-xylenol failed to show any oxygen consumption. [c] These phenols showed a sharp decrease in rate after 1 mequiv of oxygen was consumed.

hydrogen atom abstraction from phenols by diphenylpicrylhydrazyl.[12] This is in accord with our hypothesis that the rate-controlling step is *not* such an abstraction, but the reaction of Cu^I catalyst with oxygen. Another feature of the data is that a substituent favors the reaction more in the 2 than in the 4 position. For example, a 2-methyl increases the rate fourfold while a 4-methyl does so only twofold. Calculated rates (*vs.* experimental) on this basis are mesitol, 0.134 (0.130); 2,6-xylenol, 0.068 (0.068); 2-cresol, 0.017 (0.013); 4-cresol, 0.008 (0.006); and phenol, 0.004 (0.004). It is also to be noted that, while a 4-phenyl halves the rate of oxidation of phenol, a 2-phenyl doubles it.

The fact that the rate of oxygen consumption is independent of xylenol *concentration* but yet depends on the *structure* of the phenol for xylenol analogs suggests that the rate-controlling step for oxygen consumption (and thus for oxidative coupling) is the reaction of oxygen with a copper–phenol complex.

A reasonable sequence which fits with these observations is represented in Scheme I. The slow step from stage A to stage B, involving electron donation or transfer from Cu^I to molecular oxygen, would be facilitated by enhanced electron availability at the Cu^I in A. This would explain the favorable effect of electron-donor groups in the phenol. Perhaps the favorable factor of ortho substitution may be due to a steric factor which blocks excess coordination[13] of bulky solvent molecules at the Cu^I in A, permitting more ready access to the small oxygen molecule. This scheme requires that all Cu^I is rapidly and essentially quantitatively converted to a form coordinated with phenol, such as A, so that the concentration of this species is dependent on the concentration of Cu^I but *not* on the concentration of phenol as long as the latter is large compared to the Cu^I concentration. The scheme also implies that most of the copper will be rapidly reconverted to Cu^I but only slowly to Cu^{II}, so the steady state for the catalyst will be largely Cu^I.

Scheme I



Stage C would correspond to the catalyst initially formed by activation of Cu_2Cl_2 by exposure to oxygen for about 15 min.[11] The process could be envisioned as involving a Cu_2Cl_2 molecule solvated by pyridine and water (like A, but with H_2O in place of ArOH) being converted by O_2 to an analog of B, which then would react with a second molecule of solvated Cu_2Cl_2 to give two molecules of C and two of water. We have confirmed that 1 equiv of oxygen per copper atom is absorbed in this initial activation process in the absence of monomer phenol, just that required to convert Cu^I to Cu^{II}. The formulation of the oxidation of Cu^I to Cu^{II} as involving direct reaction of two cuprous atoms with a molecule of oxygen is supported by the kinetics for this process in melts, rate $= kA[Cu^+]^2[O_2]$, where A is the surface area.[14] The data were interpreted as indicating a rate-controlling process involving two cuprous ions and oxygen in the surface of the melt, producing an intermediate "peroxide" structure.

Earlier suggestions[10,11,15] of a "monomeric" copper catalyst seem to us difficult to reconcile with a rate-determining oxidation step involving simultaneous oxidation of two Cu^I to Cu^{II} by oxygen, which would require a second-order dependence on copper concentration as observed for cuprous melts.[14] One alternative would be a rate-determining step involving oxygen converting Cu^I to Cu^{III} and O_2^{2-} (or Cu^{II} and O_2^-). We prefer the view of a dimeric catalyst species.

The important role of increased base ligands at copper in promoting C–O coupling rather than C–C coupling[11,15] may depend on the decreased bonding of the aryloxy radical to copper containing more base ligands. Thus, with two pyridines per copper, the aryloxy radical formed by electron transfer will more readily dissociate as a "free" aryloxy radical and participate in the quinol ether coupling mechanism to produce C–O coupling.

With only one pyridine per copper in A′ the aryloxy radical formed by electron transfer may not be so readily released as a "free" radical. By remaining coordinated to Cu^I at oxygen, it will thus prefer to undergo C–C coupling to give B′. This can then react with oxygen through C′ to regenerate catalyst as D′ and the product 3,5,3′,5′-dimethyldiphenoquinone (Scheme II).

While Hay[15] and many others[16] have ascribed "free" free-radical mechanisms to reactions converting 2,6-xylenol by C–C coupling to diphenoquinone, Walling and Hodgdon[17]

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(12) J. C. McGowan, T. Powell, and R. Raw, *J. Chem. Soc.*, 3103 (1959).

(13) For a recent review of copper coordination chemistry, see B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, **5**, 143 (1970).

(14) D. R. Ruthven and C. N. Kenny, *Chem. Eng. Sci.*, **22**, 1561 (1967).

(15) A. S. Hay, *Fortschr. Hochpolym.-Forsch.*, 496 (1967).

(16) See, *e.g.*, S. L. Cosgrove and W. A. Waters, *J. Chem. Soc.*, 388 (1951).

(17) C. T. Walling and R. B. Hodgdon, Jr., *J. Amer. Chem. Soc.*, **80**, 228 (1958).

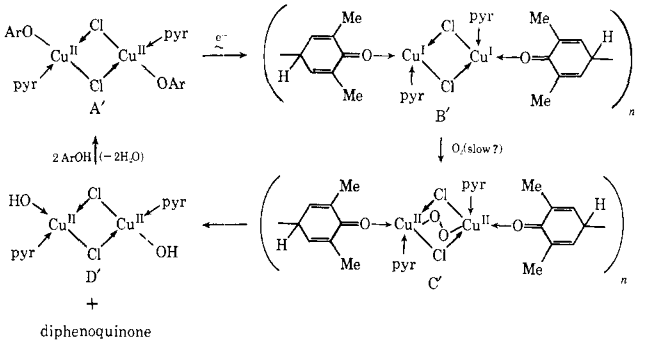
TABLE VIII

EXPERIMENTS ON DISPROPORTIONATION RATES AND STEADY STATES OF POLYXYLENOL[a]

Expt	mmol × 10^2 of Polyxylenol	Xylenol	Cu^{II}	DP_0	DP_5	DP_{20}[b]	ΔDP_{20}	$\Delta DP_{20} \cdot Cu^{II\,-1}$	DP_{eq}[c]
1	1.02	313	15.6	615	559	536	79	5.1	3.05
2	1.02	62.5	15.6	615	494	483	132	8.6	12.4
3	1.02	52.5	62.4	615	441	430	185	3.0	21.4
4	1.02	62.5[d]	15.6	615	488	478	137	8.9	13.5

[a] Polyxylenol, $[\eta] = 1.35$, 750 mg; benzene, 80 ml; pyridine, 20 ml; N_2 atmosphere; 25°. [b] DP_0 is the degree of polymerization at zero time, DP_5 at 5 min, DP_{20} at 20 min. No further decrease was observed after 20 min. The DP's were calculated from the equation $[\eta] = 3.8 \times 10^{-4} M^{0.73}$. [c] DP_{eq} is the average DP calculated for complete equilibration of polyether links, including those introduced by the Cu^{II} catalyst. [d] Xylenol dimer was used instead of the monomer.

SCHEME II



have offered much convincing evidence that this reaction, when induced by benzoyl peroxide, does *not* proceed through free radicals, as proposed by others.[16] The C–C coupling alone cannot therefore be taken as any evidence for free free-radical coupling. This does not imply that some degree of radical character may not be involved. Even the quinol ether formation may well involve radical attack on a nonradical species (*e.g.*, D), as earlier proposed for the bromine displacement polymerization to polyxylenol.[7]

Polymer–Monomer Disproportionation Kinetics

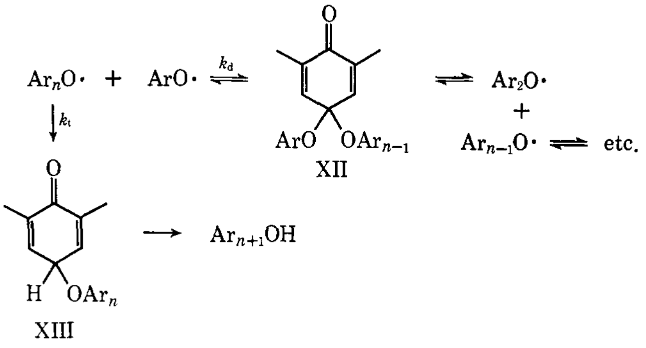
The fact that xylenol (or its dimer) and polyxylenol can undergo disproportionation under the conditions of oxidative coupling polymerization but in the absence of free oxygen has been adequately demonstrated.[18] It is clear from earlier studies that the disproportionation stops far short of the thermodynamic equilibrium and is thus a kinetically controlled process, due to the destruction of the radical centers (introduced as Cu^{II} catalyst) by termination processes. Some data supplementing the earlier reports are summarized in Table VIII. These were obtained by measuring the decrease in viscosity molecular weight of the high polymer species.

Xylenol dimer gives just as effective reduction in the molecular weight as does a molar equivalent of xylenol itself. The efficiency of depolymerization, *i.e.*, the number of units of xylenol stripped from the polymer per radical generated (Cu^{II} added) is reduced by increase in xylenol or Cu^{II} concentration (penultimate column, Table VIII). The depolymerization is clearly not thermodynamically controlled. For example, the equilibrium redistribution for experiment 1 would give polymer of DP = 3.05 compared to DP = 536 observed at the end of reaction. These results indicate, in accord with the results of others,[3,18] that redistribution is a rapid reaction but that it does not proceed to equilibrium because of radical termination reactions involving xylenol radicals reacting with xylenol or polyxylenol radicals.

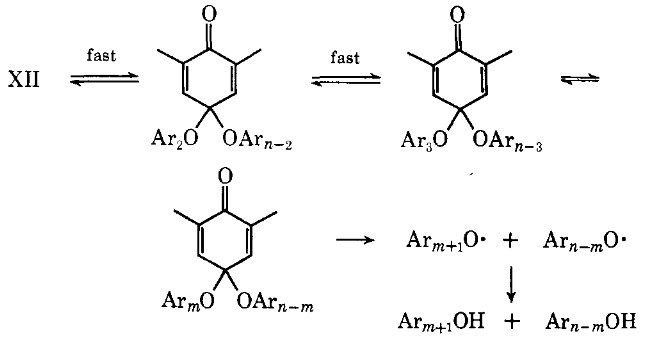
Since it has been reported that a *p*-methoxyl group enhances the rate of hydrogen atom extraction from phenol by 3250-fold,[12] it seems reasonable to assume that the 4-aryloxy radicals ($Ar_nO\cdot$ in Scheme III, $n \geq 2$) will be considerably favored over the xylenol radical ($ArO\cdot$ in Scheme III). Since this enhanced rate of formation is undoubtedly related to increased contribution of the canonical structure with the free electron on the 4 carbon of the ring, it also seems reasonable to assume that the coupling mode k_d will be favored over k_t. If k_t were the only competitive termination reaction, the ratio of disproportionation to termination would be constant. There is, however, another important termination reaction, that between two xylenol radicals to give dimer. The relative amount of monomeric xylenol radicals will be increased by either increasing the xylenol concentration or the total radical concentration (*i.e.*, the Cu^{II} catalyst added), accounting for the decreasing efficiency of disproportionation by these factors (see Table VIII).

The disproportionation data strongly support the quinone ketal fission process rather than the quinone ketal rearrangement process[3] for the case of xylenol polymerization. If the rearrangement were rapid compared to fission, then reaction of one monomer radical with a polymer radical could lead to polymer with halved molecular weight.

SCHEME III



SCHEME IV



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(18) See D. A. Bolon, *J. Org. Chem.*, 32, 1584 (1967).

TABLE IX
SYNTHESES OF 4-SUBSTITUTED XYLENOL ANALOGS

4-Substituted	Preparation	Nmr δ; ppm ($CDCl_3$)
Et	*a*	1.18 (t, 3 H), 2.22 (6 H), 2.53 (q, 2 H), 4.50 (1 H), 6.82 (2 H)
i-Pr	*b*	119 (d, 6 H), 2.18 (6 H), 2.75 (sept, 1 H), 4.40 (1 H), 6.80 (2 H)
tert-Bu	*c*	1.28 (9 H), 2.22 (6 H), 4.44 (1 H), 6.88 (2 H)
CH_2OH	*e*	2.16 (6 H), 4.31 (d, 2 H), 4.82 (t, 1 H), 6.86 (2 H), 7.95 (1 H)[d]
OCH_3	*f*	2.21 (6 H), 3.72 (3 H), 4.29 (1 H), 6.57 (2 H)
CH_2OEt	*g*	2.01 (t, 3 H), 2.10 (6 H), 3.45 (q, 2 H), 4.27 (2 H), 5.27 (1 H), 6.77 (2 H)
CHO	*h*	2.32 (6 H), 6.10 (1 H), 7.55 (2 H), 9.80 (1 H)
$COCH_3$	*a*	2.24 (6 H), 2.47 (3 H), 7.60 (2 H), 9.00 (1 H)[d]

[a] K. von Auwers and W. Mauss, *Justus Liebigs Ann. Chem.*, **460,** 240 (1928). [b] From xylenol, 2-propanol, and $ZnCl_2$, bp 86° (3 mm). *Anal.* Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.30; H, 9.62. [c] From xylenol, *tert*-butyl alcohol, and $ZnCl_2$, mp 71–73° [lit. 75°: G. Darzens, *C. R. Acad. Sci.*, **152,** 609 (1911)]. [d] In ${}^2H_6$-DMSO. [e] E. Bamberger, *Ber.*, **36,** 2028 (1903). [f] W. J. Moran, E. C. Schreiber, E. Engel, D. C. Behn, and J. L. Yamins, *J. Amer. Chem. Soc.*, **74,** 127 (1952). [g] The hydroxy methyl compound was converted to the 4-chloromethyl analog, mp 99–101° (unstable), which was immediately converted to the 4-ethoxymethyl derivative by KOH in ethanol, bp 111–113° (2 mm). *Anal.* Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.11; H, 9.05. [h] J. Thiele and H. Eichwede, *Justus Liebigs Ann. Chem.*, **311,** 363 (1900).

Since in our conditions for disproportionation at least 14.6 monoxylenol radicals were generated for each polyxylenol, most of the polyxylenol radicals must have been converted (at least temporarily) to XII. The fact that none of the disproportionations came even close to halving the molecular weight is strong evidence *against* the rapid quinone ketal rearrangement of XII (Scheme IV) and thus favors the ketal fission (Scheme III), at least under the conditions of our experiments.

Experimental Section

Infrared and nuclear magnetic resonance spectra were recorded using Perkin-Elmer Model 521 and Varian Model A-60-A instruments, respectively.

Peroxide content was measured by method II of Mair and Graupner[19] on 50–100-mg samples.

Kinetic studies were carried out in a closed system of 340 ml consisting of a 50-ml erlenmeyer flask with a magnetic stirrer connected to an oxygen reservoir and a U-tube manometer. The cuprous chloride and solvent system were added and the catalyst was preoxidized for 10–15 min to give a dark green solution, to which the xylenol or other phenol was then added with vigorous stirring; the pressure change was measured with time and converted to millimoles of oxygen consumed. The volume of oxygen consumed never changed the initial pressure by more than 4% at the end of the reaction.

Redistribution studies were carried out by preparing "catalyst" solution in pure pyridine as above, then transferring 20 ml to a sealed flask containing polyxylenol and xylenol in 80 ml of benzene under nitrogen. After specific times, 10-ml aliquots were pipetted (under nitrogen) *into a flask containing 5 ml of benzene and 0.1 ml of* acetic acid (to deactivate the catalyst). The intrinsic viscosity was then measured at 30° by pipetting 10 ml of the deactivated solution into a Ubbelohde viscometer. Dilutions were by 10 and 20 ml of benzene–pyridine solvent.

Xylenol Analogs. (1) 2,6-Dimethyl-4-(2′,6′-dimethylphenyl)-phenol (IH).[20] was prepared by mixed Grignard coupling. A mixture of 4-bromo-2,6-dimethylanisole (4.3 g, 20 mmol), 2,6-dimethylbromobenzene (7.4 g, 40 mmol), and 1.46 g (60 mmol) of magnesium turnings was refluxed in 25 ml of THF for 4 hr. The resulting solution was added to a suspension of 8.9 g (66 mmol) of finely powdered anhydrous cupric chloride in 80 ml of ether. After refluxing for 16 hr, washing, evaporation, and distillation, the 1.26-g fraction boiling from 101–142° (2 mm) and judged to be about 75% the desired unsymmetrical product from its nmr spectrum was converted to the free phenol by hydriodic acid in acetic acid. After purification by washing and distillation, IH, bp 141–146° (2 mm), was obtained: nmr (CCl_4) δ 2.01 (6 H), 2.22 (6 H), 4.41 (1 H), 6.69 (2 H), and 6.97 (3 H). *Anal.* Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02; Found: C, 84.73; H, 7.90.

When 452 mg (2 mmol) was added to a preoxidized solution of 10 mg of Cu_2Cl_2 in 7.5 ml of pyridine, 0.67 mmol of oxygen was consumed after 20 hr. The dark solution, when poured into diluted hydrochloric acid, gave 442 mg of viscous brown oil with nmr (and ir) spectra very nearly identical with the original, only two very weak new nmr bands appearing at δ 2.27 and 2.32 and the phenol OH shifting from a sharp peak at δ 4.41 to a broader peak at δ 4.68.

(2) 4-Phenoxy-2,3,5,6-tetramethylphenol (VIII). A mixture of 6.96 g (74 mmol) of phenol and 1.2 g (18.5 mmol) of 85% KOH was heated for 1 hr at 200°; then 25 mg of Cu powder, 25 mg of cupric acetate, and 4.5 g of 4-bromo-2,3,5,6-tetramethylanisole were added. After 3 hr of gentle reflux, the product was washed with 10% NaOH and recrystallized from ethanol. The methyl ether, mp 114–115°, was cleaved by HI in acetic acid to give the phenol VIII: mp 147–149°; nmr ($CDCl_3$) δ 2.05 (6 H), 2.18 (6 H), 4.53 (1 H), and 6.60–7.35 (5 H). *Anal.* Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49. Found: C, 79.27; H, 7.40.

When 363 mg (1.5 mmol) of this phenol was stirred under oxygen with 10 mg of Cu_2Cl_2 in 7.5 ml of pyridine for 20 hr, 1.2 mmol of oxygen was absorbed. Pouring into diluted hydrochloric acid gave 317 mg of yellow-brown solid: mp 60–90°; [η] 0.03; peroxide content 1.56 mequiv/g; nmr ($CDCl_3$) δ 1.4–1.8 (2.2 H), 2.03 (10.5 H), 2.18 (9.5 H), 2.30 (2.0 H), and 6.60–7.40 (10 H).

(3) 4-(4′-Bromophenoxy)-2,3,5,6-tetramethylphenol (4′-bromo-VIII) was prepared by bromination of VIII (or VIII methyl ether). It recrystallized from acetic acid–water (3:2) as white needles: mp 106–108°; nmr ($CDCl_3$) δ 2.02 (6 H), 2.18 (6 H), 4.60 (1 H), 6.63 (d, 2 H), and 7.35 (d, 2 H). *Anal.* Calcd for $C_{16}H_{17}BrO_2$: C, 59.83; H, 5.33; Br, 24.88. Found: C, 60.03; H, 5.41; Br, 24.75. From the free phenol, the first product isolated was orange needles, mp 130–132°, which proved to be a complex of 2 mol of 4′-bromo-VIII with 1 mol of duroquinone: nmr ($CDCl_3$) δ 2.02 (24 H), 2.18 (12 H), 4.60 (2 H), 6.63 (d, 4 H), and 7.35 (d, 4 H); ir ($CHCl_3$) 1590, 1640 cm^{-1} (absent in the phenol, 4′-bromo-VIII). *Anal.* Calcd for $C_{42}H_{46}Br_2O_6$: C, 62.54; H, 5.75; Br, 19.81. Found: C, 62.79; H, 5.86; Br, 19.66. The phenol could be recovered by reducing the quinone with sodium thiosulfite.

When 321 mg of this bromophenol and 65 mg of KOH in 7 ml of water, 3 ml of methanol, and 10 ml of benzene were treated with 16.5 mg of potassium ferricyanide, added with stirring over 10 min and then stirred for an additional 2 hr, the only product isolated was 285 mg of white crystals of 4′-bromo-VIII, mp 105–108°.

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(19) R. D. Mair and A. J. Graupner, *Anal. Chem.*, **36,** 194 (1964).

(20) An unsuccessful attempt to prepare this compound by Gomberg coupling of diazotized 2,6-xylidine with 2,6-dimethylnitrobenzene gave only 3-(2′,6′-dimethylphenylazo)methylindazole in 40% yield: crystals from benzene; mp 236–238°; nmr (DMSO) δ 2.42 (6 H), 2.62 (3 H), 7.20–7.35 (6 H), and 8.10 (1 H). *Anal.* Calcd for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.60; H, 6.15; N, 21.05. [E. Bamberger, *Justus Liebigs Ann. Chem.*, **305,** 289 (1899).]

Oxidation products from the xylenol analogs in Table IX were isolated after treatment of the phenols with oxygen in 15 ml of pyridine containing 20 mg of peroxidized Cu_2Cl_2. Crude product was isolated by pouring into 100 ml of dilute (5:1) hydrochloric acid.

Mesitol (IA, 816 mg, 6 mmol) consumed 3.6 mmol of O_2 in 20 hr. The crude product (617 mg, mp 108–185°) left 109 mg, mp 190–220° on benzene extraction, 0.76 mequiv of peroxide/g. *Anal.* Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 76.76; H, 7.60. Evaporation of the benzene and methanol extraction left 172 mg: mp 163–177°; $[\eta]$ 0.05 (benzene); 0.46 mequiv of peroxide/g, nmr ($CDCl_3$) δ 2.29 (3 H), 2.35 (4 H), 4.68 (1.3 H), 6.85 (0.4 H), and 7.18 (1.6 H). From the initial acid mother liquor, ether extraction yielded 167 mg, recrystallized from water as white needles (63 mg, 7%), of **4-formyl-2,6-xylenol,** mp 112–114° (lit.[21] mp 113.5–114°), identified further by comparison of the ir spectrum with that of authentic material.[21]

4-Hydroxymethyl-2,6-xylenol (IE, 608 mg, 4 mmol) consumed 2.45 mmol of O_2 in 4 hr. The crude initial precipitate, 293 mg, mp 108–145°, left 80 mg of methanol-insoluble white powder, identified as **polyxylenol:** mp 185–205°, nmr ($CDCl_3$) δ 2.09 (6 H), and 6.49 (2 H). From ether extraction of the original acid mother liquor, 185 mg (31%) of **4-formyl-2,6-xylenol,** mp 107–113°, was recovered.

4-Ethoxymethyl-2,6-xylenol (IG, 720 mg, 4 mmol) consumed 2.04 mmol of O_2 in 20 hr. There was no dilute hydrochloric acid insoluble product. Ether extraction gave 558 mg, mp 102–107°, which was recrystallized to give 438 mg (73%) of **4-formal-2,6-xylenol,** mp 110–113°, identical with authentic material[21] by ir spectra.

4-*tert*-Butyl-2,6-xylenol (ID, 534 mg, 3 mmol) consumed 2.07 mmol of O_2 in 20 hr. The crude precipitate, 496 mg, mp 110–130°, left 239 mg of methanol-insoluble amber powder, mp 168–180°, identified as an oligomer of polyxylenol by nmr ($CDCl_3$) [δ 1.33 (2.5 H), 2.09 (4 H), 2.14 (2 H), 6.47 (1.3 H), 6.98 (0.2 H), and 7.09 (0.4 H)]. Its ir spectrum ($CHCl_3$) showed no OH and only very weak C=O absorbance.

4-Methoxy-2,6-xylenol (IF, 608 mg, 4 mmol) consumed 2.9 mmol of O_2 in 20 hr. The crude amber precipitate weighed 517 mg: mp 65–90°; 1.58 mequiv of peroxide/g; nmr ($CDCl_3$) δ 1.50 (0.2 H), 1.90 (0.4 H), 2.17–2.25 (3.4 H), 3.48–3.71 (4.25 H), 4.71 (9.3 H), and 6.61–7.0 (2 H). These data are in reasonable accord with a product containing 0.25 mol of dimer peroxide per mole of *o*-quinomethane oligomer, contaminated with 1 mol of water.

Durenol (592 mg, 4 mmol) was oxidized as above but with 15 ml of benzene added. In 1 hr, 2.28 mmol of O_2 was consumed. After adding another 20 ml of benzene and extracting with hydrochloric acid, 160 mg of almost colorless white solid was filtered from the benzene layer: mp 310–345°; ir (KBr), cm^{-1} (% absorbance) 1090 (93), 1230 (96), 1360 (78), 1390 (82), 1455 (85), and 2910 (45). *Anal.* Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 79.47; H, 8.21. Further washing of the benzene fitrate, evaporation, and extraction with petroleum ether (30–60°) left 106 mg: mp 250–330°, $[\eta]$ 0.06 (benzene), nmr ($CDCl_3$) δ 1.99, ir identical with that of the insoluble polymer. Evaporation of the petroleum ether and methanol extraction gave 46 mg of duroquinone, mp 109–110° (lit.[22] 110–111°).

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(21) J. Thiele and H. Eichwede, *Justus Liebigs Ann. Chem.*, **311**, 363 (1900).

(22) L. I. Smith and F. J. Dobrovolny, *J. Amer. Chem. Soc.*, **48**, 1420 (1926).

Block-Frequency Distribution of Copolymers

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ABSTRACT: The fraction of molecules of a statistical copolymer which has a given number of blocks of specified length of one comonomer has been derived by a Markov-chain approach, while the corresponding weight fraction has been calculated by a Monte Carlo method. Attention is directed both at blocks of a given length and at blocks above a given minimum length. These quantities are of interest because the distribution of blocks which are long enough to segregate into crystalline or glassy domains governs the physical properties of block copolymers.

Copolymer properties can be profoundly influenced by the presence of blocks, *i.e.*, long sequences, of one of the constituent monomers, especially if these are long and numerous enough to segregate into separate phases of glassy or crystalline domains. Among copolymers with such long blocks, one can distinguish several types, notably block copolymers made by sequential homopolymerization (*e.g.*, ABA triblock polymers) and statistical copolymers made by conventional copolymerization with monomer concentrations and reactivity ratios which lead to block structures. This paper concerns itself only with statistical copolymers.

Many copolymers are of interest in which the molecules consist of long blocks capable of participating in glassy or crystalline domains separated by amorphous chains. The glassy or crystalline domains form tie points, *i.e.*, quasi-cross-links, which bind the amorphous chains into a network resembling that of conventionally cross-linked elastomers, and the reversible nature of such tie points confers upon some of these materials the special properties which permit their use as thermoplastic elastomers.

In statistical copolymers of this type there are some molecules which have no block long enough to participate in a glassy or crystalline domain and which are thus not tied into the network at all, while others have only one such block which does not provide any elastically effective chain, except possibly by means of chain entanglements. In order to predict the quantity of such elastically inferior molecules in the copolymer, one needs to know the block-frequency distribution, defined here as the fraction of copolymer molecules with a given number of blocks of specified length.

In a copolymer of any number of different comonomers, let us designate the monomer of interest, *i.e.*, the one capable of participating in glassy or crystalline domains, as monomer A and its sequences as A blocks. The block-length distribu-

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(1) Contribution No. 258.