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Mechanism of and Products from the Oxidation of Phenols by Hypervalent Iodine Compounds

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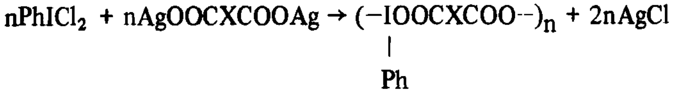
SUMMARY

Iodobenzene dichloride or diacetate initiates the polymerization of 2,6-dimethylphenolate anion to poly[oxy(2,5-dimethyl)-1,4-phenylene]. Electron spin resonance spectroscopy was used to identify the polymeric radical that is the growing chain. Infrared and NMR spectroscopy identified the final polymer. The mechanism proposed is probably applicable also to other phenol oxidation processes yielding substituted poly(oxyphenylenes).

The anomalous chemistry of those compounds of xenon, iodine, and tellurium in which the number of bonding electrons exceeds that given by Lewis valence theory has been considered in general terms by Musher [1] who coined the term "hypervalent" to describe these substances. The oxidizing properties of these compounds is in a general way similar to that of peroxides and other strong oxidizing agents, but has not been characterized in any exact fashion. We have observed [2] that the iodobenzene esters have polymeric analogs of the formula, [–I(R)OOCXCOO–], and these compounds are stable oxidizing agents (R = aryl; X = alkylene or arylene). We have been interested in determining if –I(R)OXO– compounds can be formed.

The first question to consider is the stability of bonds in –OI(R)O– compounds. Only acyl derivatives are known [3]. However, the possibility of forming alkyl or aryl derivatives should be considered. Organic compounds in which iodine has a formal valence of 3 are recognized as oxidizing agents. They are particularly used for the oxidation of glycols [4]. This background information led us to consider –I(R)OXO– compounds in which X was arylene as the most likely candidates for synthesis.

The analog reaction [2] for iodobenzene esters is



$$\mathrm{nPhCl_2 + nAgOOCXCOOAg} \rightarrow (-\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{I}}\mathrm{OOCXCOO}-)_n + \mathrm{2nAgCl} \qquad (1)$$

X = polymethylene

If X were instead arylene, there would be a possibility that $PhICl_2$ might ring-chlorinate the silver phenolate, since Neu [5] has observed this reagent to ring-chlorinate phenols. More likely would be the oxidation of the silver salt to a phenyl ether or a quinone as has been observed for phenols in the presence of iodobenzene diacetate [6, 7].

In point of fact, a series of reactions analogous to reaction (1), but with X = arylene, yielded no iodine-containing polymers.

In order to determine better the scope of reaction (1), we investigated the oxidation of phenols by iodobenzene dichloride or diacetate. Not surprisingly, this led us into a different type of polymerization, the polymerization of substituted phenols to poly(oxyphenylenes). This reaction has been discussed most extensively by Hay [8].

Our results extend the poly(oxyphenylene) reaction to a new series of oxidizing agents and provide verification of the radical nature of this polycondensation chain-reaction.

In the reaction of $PhIX_2$ (X = Cl, –OAc) with 2,6-dimethylphenolate anion, we obtained 3,3′,5,5′-tetramethyldiphenoquinone as the main coupling product (Table 1). Under certain conditions polymeric products were also obtained. In a model reaction of $PhIX_2$ and 2,4,6-tri-tert-butylphenol, we obtained a blue solution containing a stable primary radical that gave an ESR triplet signal. In our first series of experiments there was no polymer formed and we were unsuccessful in observing the signal of the secondary (polymeric) radical reported by Huymans and Waters [9].

If we increased the concentration of OH^- in the system above the equimolar ratio, we obtained a concentration of the polymeric radical that could be detected on the ESR spectrometer by the static method. This

Table 1. Typical Results from the Reaction of 2,6-Dimethylphenol with Hypervalent Iodine Compounds ($PhIX_2$)

			Products[b]		
X in $PhIX_2$	Mole ratio[a]	Solvent	Diphenoquinones	Polymer	Reaction conditions
Cl	2:1	30 EtOH:70 C_6H_6	X	–	Na phenolate
Cl	4:3	Same	X	–	Na phenolate
Cl	2:1	Tetrahydrofuran	X	–	Na phenolate
Cl	2:1	CCl_4 + 10% pyridine	X	–	1:1 Ratio of NaOH to free phenol
Cl	2:1	50 C_6H_6:50 H_2O	X	–	Same as above
OAc	2:1	Same	X	–	Same as above
OAc	2:1	Same + 25% Me_3N	X	Trace	Same as above
OAc	2:1	50 C_6H_6:50 H_2O	X	X	Ratio NaOH to free phenol > 1:1

[a] 2,6-Dimethylphenol: $PhIX_2$
[b] X = present. – = absent.

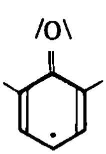
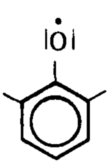
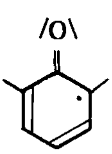
signal was identical with that published by Huymans and Waters [9], who used Ag_2O as the oxidizing agent for 2,6-xylenol. We isolated polymer from the reaction mixture by flocculating with methanol. This polymer was identified as poly[oxy(2,5-dimethyl)-1,4-phenylene] by infrared and proton resonance spectrometry (Tables 2 and 3). The polymer did not contain any iodine or chlorine. The yield of the polymer increased with increasing concentration of $PhIX_2$ and OH^- in systems as shown in Table 4.

Table 2. Infrared Assignment for Polymer from 2,6-Dimethylphenol[a]

Frequency (cm^{-1})	Intensity	Assignment
770	w	Out-of-plane bending of 2 isolated aryl hydrogens and 3 adjacent hydrogens of the polymer end group
829	w	
855	s	
1185	vs	Ether C–O ν(C–O)
3600	vw	Sterically-hindered O–H ν(O–H)

[a] All wave numbers are the values obtained after recalibration.

Some information is available concerning the stability of the radicals that may participate in the polycondensation. The $PhIX_2$ compound initiates the chain reaction by converting the 2,6-dimethylphenolate anion to a 2,6-dimethylphenoxy radical analogous to the 2,4,6-tributylphenoxy radical we actually observed in our ESR work. Buchachenko [10] has shown that the spin density of the unpaired electron is greatest in the p-position. Delocalization of the electron may be written using these resonance forms:

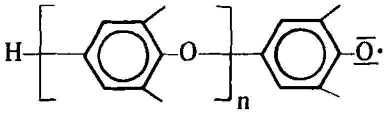
Spin density 0.45 0.20 0.29

I II III

Table 3. NMR Assignments for Polymer from 2,6-Dimethylphenol

NMR peak, ppm (τ) (relative to Me_4Si)	Relative intensity	Assignment
2.97	0.0855	H on $C_6H_3Me_2$ end group
3.57	1	H on aromatic ring $-C_6H_2Me_2-$
7.90	3	Methyl H

Huymans and Waters [9] report a 150-min half-life for the radical IV



IV

that we observed in our experiments. Therefore, the concentration of polymeric radicals will gradually increase during the coupling reaction and the rate of increase depends on the rate of initiation. When the concentration of IV is much greater than that of I-III, polycondensation will predominate over the dimerization to 3,3′,5,5′-tetramethyldiphenoquinone. Our finding that the ratio of polycondensation to dimerization increases with increased initiation rate parallels the observations of McNelis [11], who studied the oxidative coupling of 2,6-dimethylphenol in the presence of activated manganese dioxide. Greater ratios of MnO_2 to xylenol give greater ratio of polymer to quinone.

Tkáč and Kresta [10] determined the effect of the Ag_2O/2,6-dimethylphenol ratio on the rate of formation of IV. They found dimerization to predominate initially. As IV increased, as indicated by ESR spectroscopy, polymer formation took place. Our observation of the coupling reaction in the iodobenzene dichloride oxidation of 2,6-dimethylphenol leads us to believe that the mechanism presented is a general one in free-radical coupling of 2,6-dimethylphenol.

No phenol that is capable of undergoing the reaction $(ArO)^- \rightarrow (ArO)\cdot$ with hypervalent iodine can be used to form an iodine-containing polymer via reaction (1).

Table 4. Critical Experiments at 4.9 X 10^{-3} Mole Concentration of 2,6-Dimethylphenol[a]

X in $PhIX_2$	Solvent system	Mole ratio, phenol:$PhIX_2$	OH^- (mmole)	% Quinone	% Polymer insol in MeOH	Intrinsic viscosity of polymer[b] (dl/g)
Cl	B-H_2O	2:1	–	6.5	–	
Cl	”	2:1	3.75	18.1	–	
Cl	”	2:1	4.9	16.6	–	
Cl	”	2:1	7.5	17.3	4.5	0.059
Cl	”	2:1	9.8	12.9	4.1	0.065
Cl	”	2:1	19.6	10.5[c]	6.2[c]	–
Cl	”	2:1	19.6	9.2[d]	7.3[d]	0.069

Cl	B-H_2O	2:1	9.8	12.9	4.1	0.065
Cl	”	2:2	19.6	19.9	18.9	0.075
Cl	”	2:3	29.4	5.2	31.6	0.078
Cl	B-H_2O	2:3	4.9	25.6	—	
Cl	”	2:3	29.4	5.2	31.6	0.078
OAc	B-H_2O	2:1	9.8	12.1	5.7	—
OAc	”	2:2	19.6	17.2	13.0	0.085

[a] Reaction time 30 min except as noted; room temperature; 15 ml 1:2 benzene:water solvent in each experiment.

[b] Measured in chloroform at 25°C; 0.078 dl/g corresponded to a degree of polymerization of 18 by NMR and osmometry.

[c] 20 min.

[d] 85 min.

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