

Ab Initio Calculations on 2,6-Dimethylphenol and 4-(2,6-Dimethylphenoxy)-2,6-dimethylphenol. Evidence of an Important Role for the Phenoxonium Cation in the Copper-Catalyzed Oxidative Phenol Coupling Reaction

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Abstract: *Ab initio* unrestricted Hartree–Fock calculations with a 6-31G* basis set were performed on 2,6-dimethylphenol (DMP or monomer) and 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol (dimer) to gain more insight into the mechanism of the copper-catalyzed oxidative phenol coupling reaction. Atomic charges were determined for the phenol, phenoxyl radical, phenolate anion and phenoxonium cation (both the singlet and triplet state) of both species. Calculations for the monomer show that the only aromatic carbon atom bearing a partial positive atomic charge is the *para* carbon of the cation in the singlet state. In the case of the dimer, the presence of a *p*-phenoxy substituent results in a partial positive charge for the *para* carbon of the first aromatic ring in all states, but this charge is significantly higher for the singlet cation. In the singlet cationic state, the *para* carbon of the first aromatic ring is therefore the site most susceptible to nucleophilic aromatic substitution. This result strongly supports a proposal for the mechanism of the copper-catalyzed oxidative phenol coupling, in which dinuclear phenolate-bridged copper(II) species act as intermediates affording phenoxonium cations after a double one-electron transfer. Furthermore, the charges in the second aromatic ring of the dimer are hardly, -if at all, influenced by the overall electronic state of the molecule. The charge in the first ring cannot pass the ether bond. This result, combined with the observation that the *para* carbon of the first aromatic ring of the singlet cation bears a large positive charge, favors a mechanism where quinone ketals are formed as intermediates during the coupling of oligomeric phenols.

Introduction

The oxidative coupling of phenols, as shown schematically in Figure 1 for 2,6-dimethylphenol (DMP), is known to be catalyzed by copper–amine complexes.¹ The two main products of this reaction are an intensely colored diphenoquinone (DPQ²), arising from C–C coupling of two phenol moieties and a C–O coupled product that can react further and will ultimately yield a polymer, the linear poly(phenylene ether) (PPE), in high yield and of high molar mass. Other products are not formed in significant amounts.³ The resulting polymer shows very good mechanical properties and chemical stability, even at elevated temperatures, and is therefore an important engineering plastic.^{4,5} The other product, DPQ, which is formed in less than 5% yield under normal conditions, may degrade the polymer upon further processing at high temperatures, and must be removed. Consequently, processes that result in low yields of DPQ are required, and therefore understanding of the reaction mechanism is crucial.

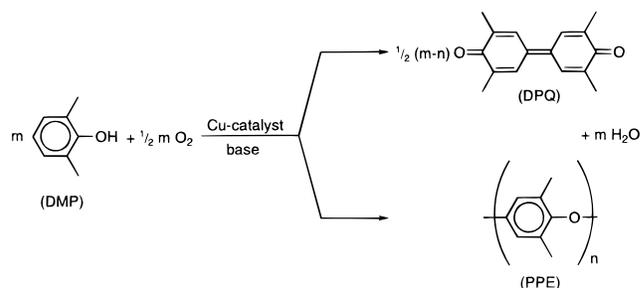


Figure 1. Overall reaction scheme for the oxidative coupling of DMP to PPE and DPQ.

The mechanism of this reaction, especially with respect to the phenol oxidation step and the subsequent phenol coupling step, has been the subject of much discussion during the last decades, and several mechanistic proposals have been made accordingly.^{4,6–12} These proposals include the coupling of DMP by a radical pathway (free or coordinated) or by an ionic mechanism, both for C–O and C–C coupling. Recently a kinetic and spectroscopic investigation into the mechanism of

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this reaction was performed,¹³ the results of which support a mechanism where dinuclear phenoxo-bridged copper species play an important role. It is thought that such dinuclear species will afford phenoxonium cations after a double one-electron transfer.

To obtain more insight into the actual phenol coupling step and thus to be able to distinguish between the mechanistic proposals, *ab initio* unrestricted Hartree–Fock calculations were performed with a 6-31G* basis set on DMP itself and its deprotonated derivatives, *i.e.* the phenolate anion, phenoxy radical, and phenoxonium cation (both singlet and triplet states). Emphasis was put on the calculation of the atomic charges within the different species in order to identify the most likely coupling pathway between a phenol (or phenolate) and an oxidized phenolic species. To investigate the effect that a *p*-phenoxo substituent has on the atomic charges, these calculations were also performed for the C–O coupled dimer of DMP, 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol. These calculations may also provide more insight into the coupling mode of oligomeric phenols.

Computational Methods

All calculations were performed on a Silicon Graphics Iris Indigo system with the Spartan set of programs.¹⁴ In all cases the *ab initio* unrestricted Hartree–Fock (UHF) method was used,¹⁵ both for open and closed shell species. Use of the UHF method for open shell species can lead to contamination of the wave function with functions corresponding to states of higher spin multiplicity.¹⁶ Where applicable expectation values of $\langle S^2 \rangle$ are given.

Calculations were initiated with a small set of orbitals (STO-3G) to perform preliminary geometry optimizations. The optimized structure from these calculations was subsequently used to start a calculation with a bigger basis set (3-21G), the data of which were used to start the final calculation with use of a 6-31G* basis set, with which the final coordinates, natural atomic charges, and electron and spin density maps were calculated. Natural population analysis was preferred over Mulliken analysis, because it affords better results and is less sensitive to the basis set used.¹⁷

Results and Discussion

The final structures of both the monomer and dimer phenol are shown in Figures 2 and 3, respectively, together with the adopted numbering scheme. In the case of the monomer it is noteworthy that the OH bond is coplanar with the aromatic ring and that the methyl groups are in a position that gives minimal overlap with the hydroxyl group. Both structural features are consistent with the X-ray structure of DMP.¹⁸ A comparison of the calculated and experimentally found¹⁸ bond distances and angles between the non-hydrogen atoms, given in Table 1, shows that the calculated and experimental structures are in good agreement. The calculated coordinates of the non-hydrogen atoms of the monomer phenol are listed in Table 2. The natural atomic charges for all the calculated states of the monomer are listed in Table 3. The calculated charges of the phenoxonium singlet and triplet species are (qualitatively) in agreement with similar calculations which were performed on an unsubstituted phenoxonium cation, albeit with a much smaller basis set (STO-3G).¹⁹

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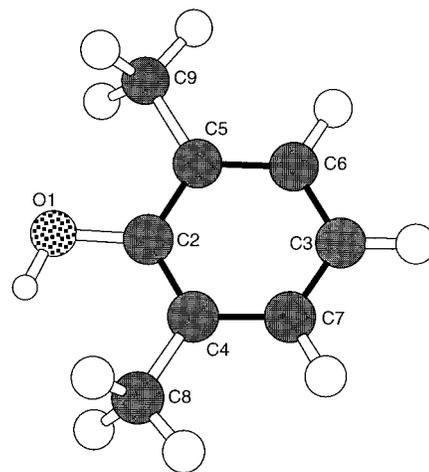


Figure 2. Calculated (UHF, 6-31G* basis) structure of DMP together with the numbering scheme adopted.

Table 1. Comparison of Experimental¹⁸ and Calculated (UHF, 6-31G* Base) Bond Distances (Å) and Angles (deg) between the Non-Hydrogen Atoms of DMP

	exptl ¹⁸	calcd		exptl ¹⁸	calcd
O1–C2	1.37	1.359	O1–C2–C5	116.8	116.15
C2–C4	1.38	1.391	C2–C4–C7	116.7	118.12
C2–C5	1.40	1.393	C2–C4–C8	122.4	120.77
C3–C6	1.36	1.386	C2–C5–C6	118.9	118.03
C3–C7	1.39	1.381	C2–C5–C9	121.0	119.92
C4–C7	1.38	1.390	C3–C6–C5	119.5	121.31
C4–C8	1.50	1.513	C3–C7–C4	121.3	121.16
C5–C6	1.37	1.385	C6–C3–C7	120.9	119.41
C5–C9	1.48	1.509	C6–C5–C9	120.1	122.05
C2–O1–H13	109.7	111.28	C7–C4–C8	120.9	121.11
O1–C2–C4	120.5	121.88			

Table 2. Calculated Cartesian Coordinates for the Non-Hydrogen Atoms of DMP

	x	y	z
O1	–2.0050	–0.0212	–0.1276
C2	–0.6503	–0.0070	–0.0235
C3	2.1087	0.0226	0.0520
C4	–0.0085	–0.0070	1.2101
C5	0.0577	0.0076	–1.2235
C6	1.4410	0.0222	–1.1628
C7	1.3813	0.0081	1.2255
C8	–0.8041	–0.0229	2.4964
C9	–0.6862	0.0070	–2.5365

Table 3. Calculated Values for $\langle S^2 \rangle$ and Natural Atomic Charges of Selected Atoms of DMP, *i.e.*, the Phenol, Phenolate Anion, Phenoxy Radical, and the Phenoxonium Cation^a

	phenol ($S = 0$)	anion ($S = 0$)	radical ($S = 1/2$)	cation ($S = 0$)	cation ($S = 1$)
$\langle S^2 \rangle$	0	0	1.3500	0	2.1614
O1	–0.76	–0.88	–0.47	–0.44	–0.32
C2	0.39	0.52	0.41	0.55	0.25
C3	–0.25	–0.39	–0.18	0.19	–0.33
C4	–0.12	–0.20	–0.02	0.18	0.16
C5	–0.09	–0.20	–0.02	0.18	0.16
C6	–0.20	–0.19	–0.24	–0.37	0.02
C7	–0.20	–0.19	–0.24	–0.37	0.02
C8	–0.66	–0.61	–0.65	–0.69	–0.70
C9	–0.64	–0.61	–0.65	–0.69	–0.70

^a The overall spin state is given between brackets.

In the case of the dimer phenol, the OH bond is also coplanar with the aromatic ring to which it is connected. The planes of

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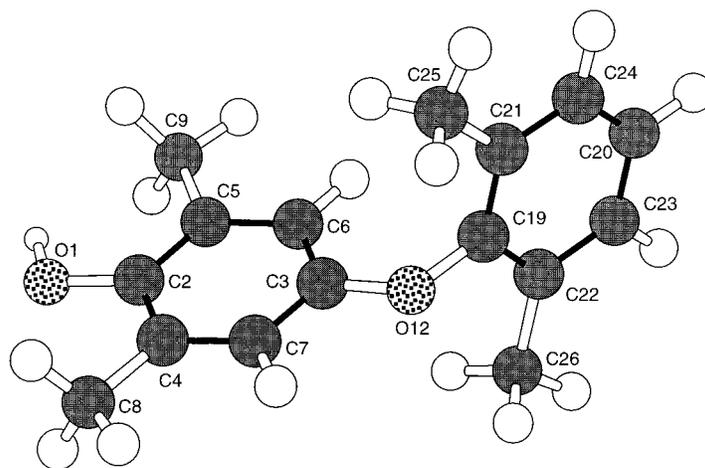


Figure 3. Calculated (UHF, 6-31G* basis) structure of dimer DMP, together with the numbering scheme adopted.

Table 4. Calculated Cartesian Coordinates for the Non-Hydrogen Atoms of Dimer DMP

	x	y	z		x	y	z
O1	-4.2482	0.2586	1.2133	O12	1.2151	0.0535	0.7648
C2	-2.9002	0.1990	1.0216	C19	1.9059	-0.1008	-0.4122
C3	-0.1511	0.0935	0.7772	C20	3.3918	-0.4049	-2.7032
C4	-2.1084	0.3042	2.1660	C21	2.3110	1.0364	-1.1006
C5	-2.3341	0.0433	-0.2309	C22	2.2404	-1.3849	-0.8248
C6	-0.9439	-0.0089	-0.3445	C23	2.9888	-1.5180	-1.9871
C7	-0.7369	0.2495	2.0262	C24	3.0581	0.8619	-2.2581
C8	-2.7589	0.4733	3.5165	C25	1.9559	2.4114	-0.5878
C9	-3.2034	-0.0692	-1.4638	C26	1.8102	-2.5869	-0.0187

the two aromatic rings are perpendicular with respect to each other, the dihedral angles around the ether bond being 179.9° (C7–C3–O12–C19) and -91.9° (C3–O12–C19–C22), which is also the case for the radical and cationic species. In the case of the anion, however, these values differ. The planes of the aromatic rings are still perpendicular to each other, but both rings are rotated about their respective C–O12 bonds. In this case the values obtained for the dihedral angles around the ether bond are as follows: 141.5° (C7–C3–O12–C19) and -68.0° (C3–O12–C19–C22). It is not clear what causes this difference. The calculated coordinates of the non-hydrogen atoms of the dimer phenol are listed in Table 4. The natural atomic charges for all the calculated states of the dimer are listed in Table 5.

It is noted that the calculations described were performed for the metal-free species. It is realized that for more realistic results, the coordination to copper (complete with ligands²⁰) should be taken into account. Such considerations, however, imply a different level of calculations, requiring much longer processing times, which were not performed as yet. Although the atomic charges are expected to vary somewhat upon coordination of the phenolic species to copper, the qualitative picture is unlikely to change drastically upon coordination to copper. Therefore, it is believed that the current results can be extrapolated to the catalytic reaction.

As mentioned in the introduction, several possible pathways, both radical and ionic, have been proposed for the mode of action of coupling of two phenol moieties, as shown in Scheme 1. It should be noted that instead of phenols, phenolate anions may also react with the oxidized species. If one considers the calculated atomic charges of the monomeric species, it is obvious that the electrophilic pathway for C–O coupling, as shown in Scheme 1b,^{21,22} is not a viable option, since it would

Table 5. Calculated Values for $\langle S^2 \rangle$ and Natural Atomic Charges of Selected Atoms of the Dimer, i.e., Phenol, Phenolate Anion, Phenoxy Radical, and Phenoxonium Cation^a

	phenol ($S = 0$)	anion ($S = 0$)	radical ($S = 1/2$)	cation ($S = 0$)	cation ($S = 1$)
$\langle S^2 \rangle$	0	0	1.7838	0	2.9204
O1	-0.76	-0.88	-0.48	-0.49	-0.40
C2	0.35	0.50	0.40	0.58	0.38
C3	0.35	0.20	0.38	0.74	0.34
C4	-0.05	-0.17	-0.02	0.09	0.01
C5	-0.09	-0.17	-0.01	0.12	0.01
C6	-0.30	-0.26	-0.30	-0.39	-0.27
C7	-0.26	-0.24	-0.26	-0.35	-0.27
C8	-0.64	-0.62	-0.65	-0.68	-0.66
C9	-0.65	-0.62	-0.65	-0.68	-0.66
O12	-0.61	-0.63	-0.61	-0.52	-0.52
C19	0.33	0.38	0.33	0.26	0.65
C20	-0.22	-0.25	-0.22	-0.18	-0.08
C21	-0.05	-0.07	-0.05	-0.04	0.01
C22	-0.05	-0.06	-0.05	-0.04	-0.04
C23	-0.23	-0.23	-0.22	-0.22	-0.20
C24	-0.23	-0.23	-0.22	-0.22	-0.22
C25	-0.64	-0.63	-0.65	-0.65	-0.67
C26	-0.64	-0.64	-0.65	-0.65	-0.67

^a The overall spin state is given between brackets.

require the attack of a cation with a positively charged oxygen atom on the *para* carbon of DMP or its anion. Consequently, this scheme is not in agreement with the preference for C–O coupling (>95% selectivity) of the reaction under good conditions.²³ Furthermore, should this be the right pathway, then oxygen-protected species, like the methyl ether of DMP, 2,6-dimethylanisole, should also be incorporated into the products by attack of the cation on the *para* carbon of such a species. However, such a reaction has never been observed experimentally.^{4,5,24}

Therefore, the actual mechanism must involve the nucleophilic attack of a phenol or phenolate on some oxidized phenolic species. Evidently, the species most susceptible to this kind of attack is the one that has the highest positive charge on the *para* carbon of the phenol aromatic ring, since the oxygen atom always bears a (partial) negative charge. This negative charge is not in agreement with the calculated charges of the unsubstituted phenoxonium cation, where the oxygen atom bears a positive charge in the triplet state.¹⁹ However, a much lower

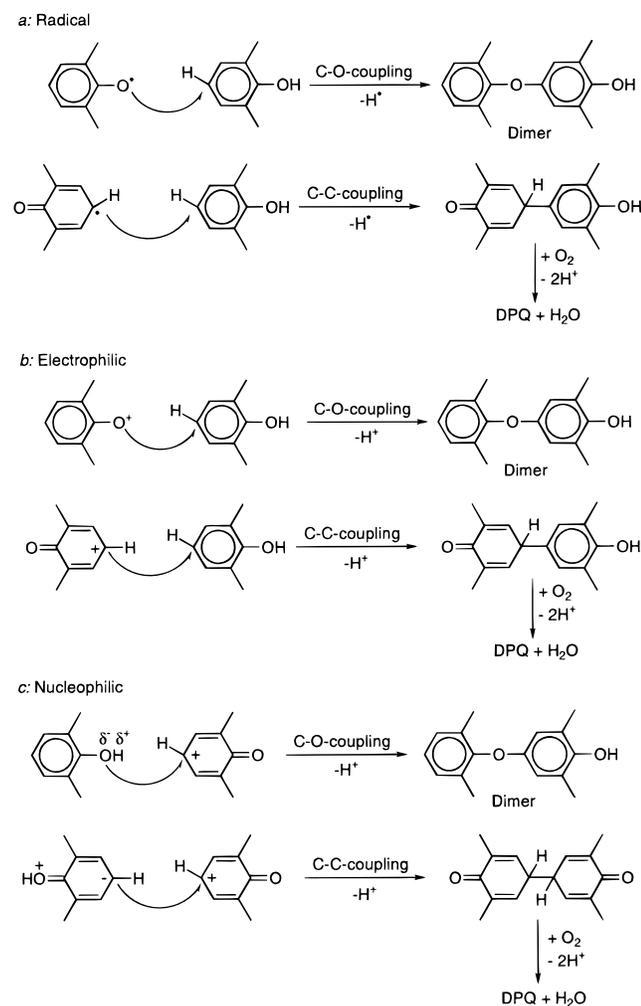
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Scheme 1. Mechanistic Pathways Proposed for the Oxidative Coupling of DMP

level of calculation (STO-3G) was employed here and Mulliken charges were used, which probably explains this difference. It is clear, from the calculated charges of the monomeric species, that the only state with a positive charge on the *para* carbon (C3) is the cation in the singlet state. Note that in this singlet state also the *ortho* carbons (C4 and C5) and the *ipso* carbon (C2) bear a partial positive charge, all of which are sterically less accessible for coupling because of the *o*-methyl groups.

On these grounds the radical does not seem to be a very likely candidate for attack by or on a phenol or phenolate, although atomic charges are not the only thing to consider here as the unpaired electron of the radical is the most important factor governing the reactivity. It is known that the treatment of DMP with a radical initiator, like benzoyl peroxide, mainly yields DPQ,^{25,26} whereas in the copper-catalyzed reaction less than 5% DPQ is formed under optimal conditions. Therefore the radical pathway as shown in Scheme 1a^{4,27,28} is quite unlikely.

These results obviously favor the phenoxonium cation over a phenoxyl radical as the key intermediate species. This strongly supports a mechanistic proposal, which involves the formation of a phenolate-bridged dinuclear copper(II) species as the catalytically active intermediate.^{12,13,21} This bridging phenolate

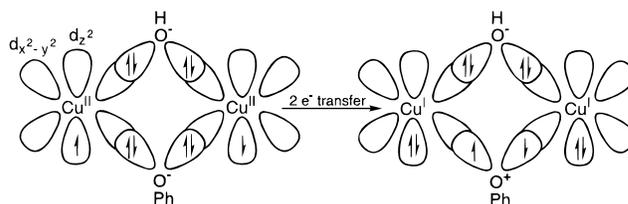


Figure 4. Simplified orbital representation of the two-electron phenol oxidation within a (μ -phenoxo)(μ -hydroxo)-dicopper(II) species.

may experience a 2-electron oxidation, resulting in a phenoxonium cation that is possibly still coordinated to the (dinuclear) copper(I) species, as its oxygen atom still bears a partial negative charge. The cation can then be attacked by a phenol (as shown in Scheme 1c) or by a phenolate to give either the bisphenol that will afford DPQ or the dimer phenol that may react further and will ultimately afford the polymer PPE.

The calculated data clearly show that the singlet cation is a likely subject for nucleophilic attack on its *para* carbon. The triplet cation on the other hand is definitely not a target, since the *para* carbon bears a partial negative charge. It is not immediately obvious which one of the cationic species will be formed after the 2-electron oxidation of a phenolate anion. It can be argued, however, that in the case of a dinuclear (μ -phenoxo)(μ -hydroxo)-bridged copper(II) catalytic intermediate, as proposed from earlier work,¹³ the copper ions are almost certain to be strongly antiferromagnetically coupled.²⁹ This means that the unpaired electrons on the copper ions will have opposite spins. It stands to reason that after the double one-electron oxidation of the phenolate, the transferred electrons will form electron pairs with the unpaired electrons of the copper ions, as shown schematically in Figure 4. To make this possible these transferred electrons must have opposite spins. Therefore the overall spin state of the bridging phenolate ($S = 0$) will not change upon being oxidized to the cation. So, it can be concluded that the phenoxonium cation formed in this reaction will be in the singlet state.

In the case of the dimer, which can also be used as a model for higher oligomers, the situation is slightly different. Here the *para* carbon of the phenolic aromatic ring (C3) bears a partial positive charge in all states due to the phenoxo substituent, but this charge is much higher, *viz.* 0.74, for the singlet cation than for any of the other states. So, as in the case of the monomer, the singlet cation of the dimer is also the species most susceptible to nucleophilic attack. The argument, why the singlet cation is likely to be formed in the case of the monomer phenol (*vide supra*), is also valid for the oligomeric phenols.

Another factor of interest is also obvious from the calculated charges of the dimer. The atomic charges in the second aromatic ring (the one not bearing the phenol functionality) are not or only barely influenced by the overall charge of the molecule. Apparently the molecular charge resides completely on the first aromatic ring and cannot pass the ether bond. This was also found from an EPR study on the radical of 4-(phenoxy)-2,6-di-*tert*-butylphenol.³⁰

On the basis of these findings, the most probable scheme for C–O coupling of oligomeric phenols can now be deduced. Three possibilities have been recognized, as depicted in Scheme 2 for the dimer phenol. Pathway a in Scheme 2 is the electrophilic one, similar to the one described for the monomer phenol. This pathway has the appealing feature that the coupling of oligomeric phenols is very straightforward: a phenoxonium

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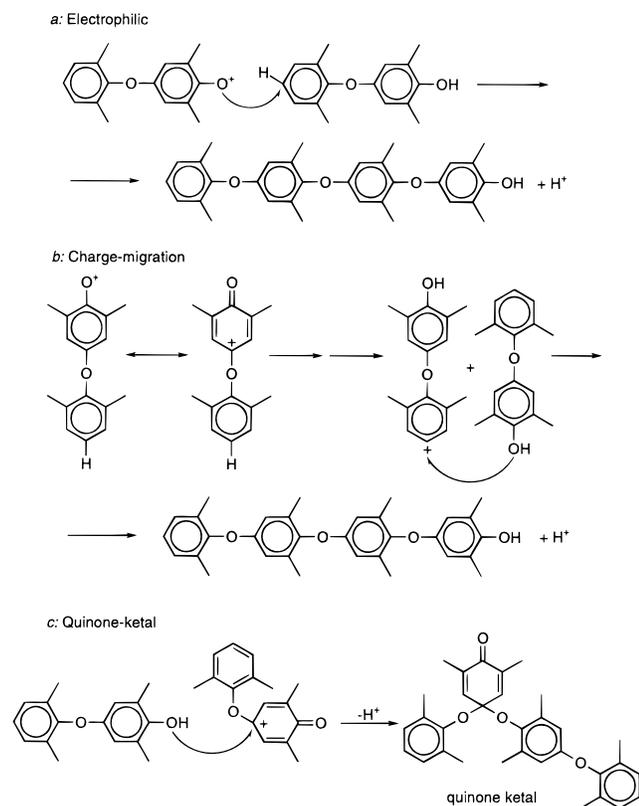
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Scheme 2. Mechanistic Pathways Proposed for the C–O Coupling of Dimer DMP

cation just attacks the *para* carbon of the terminal aromatic ring of an oligomeric phenol. It does not matter how long the chain is that trails behind the cation or how long the attacked oligomeric phenol is, since it is the terminal aromatic ring that is being attacked. However, this pathway can be discarded on the same grounds as in the case of the monomer (*vide supra*).

The second pathway (b in Scheme 2) is of the nucleophilic type and shows that the positive charge of the phenoxonium cation migrates down the PPE chain via the ether linkages, eventually ending up in the terminal aromatic ring. Then the *para* carbon atom of this ring can be attacked by a (oligomeric) phenol or phenolate. This pathway is actually an adaptation of a similar pathway proposed for a radical mechanism.^{31,32} The attractiveness of this pathway is the same as that of the electrophilic pathway described above: the simple, straightforward coupling of oligomeric phenols. Unfortunately, it has been shown that the charges in the second aromatic ring of the dimeric species are not or only barely influenced by the overall electronic state of the molecule. The charge resides almost exclusively on the aromatic ring bearing the phenol functionality. So, as the charge from one aromatic ring does not pass the ether bond to another aromatic ring, the pathway depicted in Scheme 2b cannot be correct.

Pathway c in Scheme 2 is the only one that is in agreement with all our findings. In this pathway C–O coupling of two dimeric phenols occurs by nucleophilic attack of the oxygen

atom of a phenol or phenolate of one of the dimers onto the *para* carbon of the first aromatic ring of the cation (in the singlet state), whereby a quinone ketal is formed. This ketal may then undergo rearrangement to form the tetramer, or may split off one of the phenoxo substituents to give either two dimers or a trimer and a monomer species. The existence of such a quinone ketal intermediate has been proposed from several experimental studies regarding the product distribution.^{31,33–36} One of the observations was that when starting from dimer phenol after a short reaction time monomer DMP formed. This redistribution can only be explained by assuming the existence of a quinone ketal as an intermediate.

Conclusions

Unrestricted Hartree–Fock *ab initio* calculations of atomic charges performed on the phenol, the phenolate anion, the phenoxy radical, and the phenoxonium cation (both singlet and triplet states) of 2,6-dimethylphenol and its dimer, 4-(2,6-dimethylphenoxy)-2,6-dimethylphenol, provide supporting evidence for a mechanistic proposal for the copper-catalyzed oxidative coupling of 2,6-dimethylphenol where phenoxonium cations are proposed as key intermediates.

The only possible coupling mode that explains the high selectivity for C–O coupling is a nucleophilic attack of a phenol or phenolate on the *para* carbon of a phenoxonium cation. Electrophilic and radical pathways have been ruled out. The cation needs to be in the singlet state to be susceptible to nucleophilic attack, which is in agreement with a mechanistic proposal where the phenoxonium cations are formed by a double 1-electron transfer within an antiferromagnetically coupled, phenoxo-bridged dinuclear copper(II) complex from the bridging phenolate to both copper(II) ions.

The atomic charges within the second aromatic ring (not bearing the phenol functionality) of the dimer are not or only barely influenced by the overall electronic state of the dimer species. The charge resides almost exclusively in the first phenoxy residue, and does not cross the ether bond. This observation, combined with the fact that the *para* carbon of the first aromatic ring of the dimer in the singlet cationic state is the site most susceptible to nucleophilic attack by a phenol or phenolate, favors a mechanism for the C–O coupling of oligomeric phenols where quinone ketals are formed as intermediates.

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Supporting Information Available: A listing of the calculated coordinates and energies (UHF) of the phenolic, anionic, radical, and cationic species of both monomer DMP and dimer DMP (12 pages). See any current masthead page for ordering and Internet access instructions.

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