

Role of (μ -Oxo)dicopper(III) Complexes in Oxidative Polymerization of Phenol. A DFT Study

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Received March 2, 2003; Revised Manuscript Received May 14, 2003

ABSTRACT: A detailed quantum mechanical study of the generation of “controlled” radical species participating in regioselective polymerization of phenol has been carried out at the GGAI/LACVP* level of theory. There are two pathways of “controlled” radicals generation which represent phenol radicals stabilized by Cu(I)–amine complexes, postulated as active species in regioselective polymerization of phenol. One of them is the proton abstraction from phenol–Cu(II)–amine complexes by organic base available in the reaction mixture while the other is the hydrogen abstraction by (μ -oxo)dicopper(III) complexes from Cu(I)–phenol complexes. According to calculations μ - η^2 : η^2 -peroxodicopper(II) complexes originally postulated as precursors for generating of “controlled” radicals are incapable of their generation. It seems it is (μ -oxo)dicopper(III) complexes that are responsible for “radical controlled” oxidative polymerization of phenol.

Introduction

Oxidative polymerization of phenols catalyzed by a metal complex or an enzyme^{1–7} is one of the “green chemistry” processes where reaction conditions are mild and the only byproduct is water. One of the important problems in the oxidative polymerization of phenol is the branching due to the fact that both ortho and para positions are active in polymerization. 2,6-Disubstituted phenols produce linear polymers. Thus, poly(2,6-dimethyl-1,4-phenyleneoxide) is an important engineering plastic widely used in industry.⁸

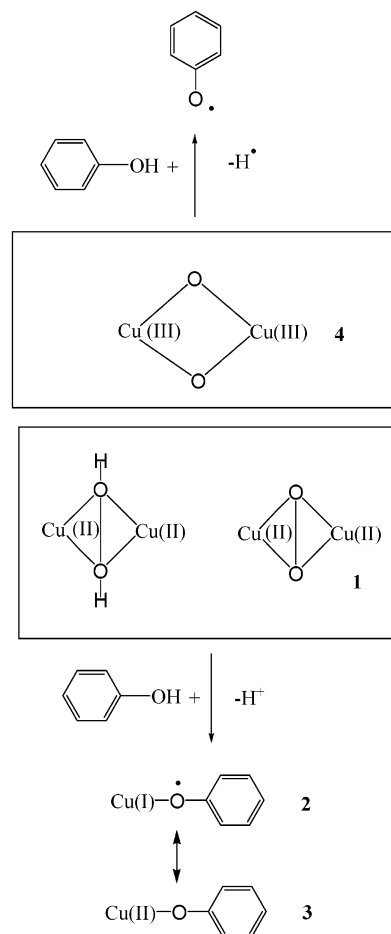
Direct synthesis of poly(1,4-phenyleneoxide) starting from phenol has been an attractive target for a long time.^{2,6,9} Despite numerous efforts, no reports on successful regioselective oxidative polymerization of 2,6-unsubstituted phenols has been published until recently when Higashimura et al. reported very elegant “radical controlled” oxidative polymerization of 4-phenoxyphenol by tyrosinase model complex catalyst to give poly(1,4-phenyleneoxide).^{10,11}

The working hypothesis explaining the regioselectivity of “radical controlled” oxidative polymerization is based on the formation of “controlled” radicals (Scheme 1). μ - η^2 : η^2 -Peroxodicopper(II) complex **1** abstracts proton from phenol to give phenoxocopper(II) complex **2** which is equivalent to phenoxy radical-copper(I) complex **3**.

On the other hand electrophilic bis(μ -oxo)dicopper(III) complex **4** abstracts a hydrogen atom from phenol, generating free phenoxy radicals which are much more active compared to “controlled” radical **3** and, therefore, less selective.

Thus, high regioselectivity of tyrosinase model complexes is explained by the generation of mostly μ - η^2 : η^2 -peroxodicopper(II) complex **1** which is capable of “controlled” radicals **3** formation while electrophilic (μ -oxo)dicopper(III) complex **4** gives “free” phenoxy radicals

Scheme 1. Originally Proposed Scheme for Generation of Free and “Controlled” Radicals According to ref 11



having low regioselectivity.¹¹ On the other hand, experimental observations¹² and theoretical calculations¹³ show fast and reversible isomerization between μ - η^2 : η^2 -peroxodicopper(II) and (μ -oxo)dicopper(III) complexes.

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Moreover, they are almost isoenergetics which means perceptible concentration of (μ -oxo)dicopper(III) complexes in the reaction mixture generating free phenoxy radicals thus interfering “controlled” polymerization of phenols.

The aim of this paper is to study the mechanism of “controlled” oxidative polymerization of phenols using quantum chemistry tools and to propose a new mechanism of generating “controlled” radicals in agreement with above-mentioned observations.

Computational Details

All calculations were carried out with Jaguar v 4.2 program.¹⁴ The geometry optimizations were run using density functional theory (DFT) at general gradient approximation (GGAI/LACVP* level of theory) which is successful in modeling energetics, structures, and spectroscopy of transition metal systems.¹⁵ The LACVP* basis set uses standard 6-31G* basis set for valence and outermost set of core electrons of third row and heavier elements and LAC pseudopotential¹⁶ for inner core electrons. The elements of the first and second rows uses standard 6-31G* basis set. Frequency calculations were run for all structures to make sure that a transition state (one imaginary mode) or a minimum (zero imaginary modes) is located. The Poisson–Boltzmann solver^{17,18} implemented in Jaguar v 4.2 was used to calculate the solvation effects on the studied molecules in toluene at GGAI/LACVP* level of theory. In other words, the structures have not been reoptimized in the presence of solvent since it has been shown previously that reoptimization has very limited effect on the computed energies.^{19–23} The GGA functional was shown to reproduce reasonably well the geometry and the energetics of Cu(II)–Cu(III) complex transformation.¹³ For the processes where the number of particles do not change during the reaction, the energetics effect calculated on the basis of total electronic energies is very close to the Gibbs free energies. In cases where the number of particle changes during the reaction and entropy contribution are of importance, exact Gibbs free energies at 298.15 K were calculated.

Results and Discussion

Radical-controlled oxidative polymerization is carried out in nonpolar solvents like toluene or THF the presence of 2,6-diphenylpyridine (DPP), Cu(I), or Cu(II) amine complexes and molecular oxygen. Bi- and tridentate ligands are used. Among them are *N,N,N',N'*-tetraethylethylenediamine and 1,4,7-trisubstituted-1,4,7-triazacyclononane.^{10,11} The calculations were carried out with both bi- and tridentate ligands. As a model for bidentate ligand was chosen *N,N,N',N'*-tetramethylethylenediamine, while 1,4,7-trimethyl-1,4,7-triazacyclononane was used as tridentate ligand. It has been shown that ligand play very important role in the fine-tuning balance between μ - η^2 : η^2 -peroxodicopper(II) and (μ -oxo)-dicopper(III) complexes; therefore, the inclusion of realistic ligands and solvation effects in theoretical treatment is essential for quantitative description of reaction energetics.

According to ref 24, Cu–Cu and Cu–O experimental distances and Cu–O–Cu experimental angles vary in (μ -oxo)dicopper(III) complexes in the ranges 2.59–2.91 Å, 1.8–1.94 Å, and 92.5–103.2°, respectively, depending on the ligand nature. In the case of optimized structures **5a** and **5b**, these values were 2.80 Å, 1.83 Å, and 99.7° and 2.84 Å, 1.84 Å, and 100.8°, respectively. The corresponding values in μ - η^2 : η^2 -peroxodicopper(II) complexes **9a** and **9b** were found to be 3.60 Å, 1.95 Å, and 135.1° and 3.67 Å, 1.99 Å, and 136°, respectively.

Table 1. Gas Phase Total Electronic Energy (*E*), Gibbs Free Energy at 298.15 K (*G*), and Solvation (*E_s*) Energy (au) Calculated at the GGAI/LACVP* Level of Theory

intermediate	<i>E</i>	<i>G</i>	<i>E_s</i>
5a	–1237.579383		–0.134500
5b	–1581.600442		–0.125257
6a	–851.010801	–850.730644	–0.042071
6b	–1023.020193	–1022.659966	–0.039999
7a	–1237.728432		–0.295932
7b	–1581.788327		–0.276490
PhOH	–307.337677	–307.264504	–0.005737
PhO [–]	–306.761636		–0.058485
8a	–850.608550		–0.012908
8b	–1022.605411		–0.009721
9a	–1237.571496	–1237.170721	–0.133225
9b	–1581.602900	–1581.048753	–0.122229
10a	–1237.690457		–0.288442
10b	–1581.762029		–0.270753
11a	–850.636985	–850.356039	–0.149958
11b	–1022.668746	–1022.306368	–0.143583
12a	–850.411565		–0.041115
12b	–1022.422015		–0.040000
DPP	–710.103781		–0.005010
DPP ⁺	–710.496632		–0.041115
13a	–1238.212080		–0.133863
13b	–1582.237961		–0.124938
14a	–1238.164886		–0.132110
14b	–1582.199754		–0.123026
PHO [•]	–306.702440		–0.006693
TRa	–1237.563260		–0.134022
TRb	–1581.590025		–0.123504
15	–613.486049		–0.007649
16	–612.911680		–0.051295
17	–612.849398		–0.007649
18a	–543.628933	–543.442584	–0.046852
18b	–715.646144	–715.380817	–0.042230
19a	–543.199126	–543.014756	–0.182627
19b	–715.253199	–714.998343	–0.164300
O ₂	–150.281628	–150.297087	–0.000527

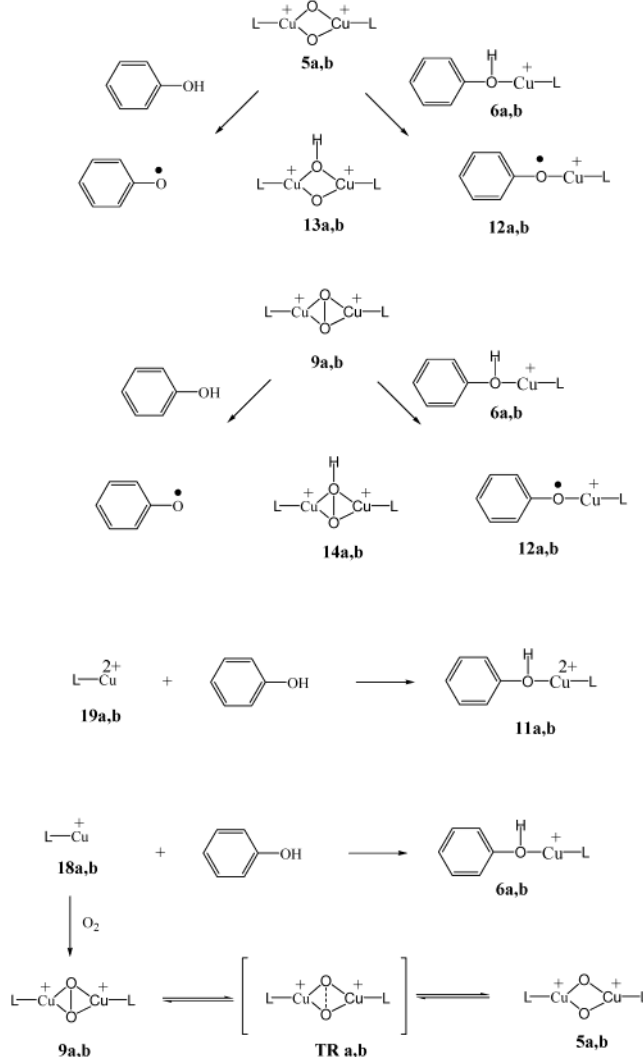
Table 1 shows total electronic, Gibbs free, and solvation energies for all studied molecules while Schemes 2–5 show the studied reaction pathways.

Among them are the reactions leading to the formation of “controlled” radicals **12a,b** (Schemes 2 and 3).

The most straightforward way of generating “controlled” radicals **12a,b** is the reaction of Cu(II) amine complexes **19a,b** with phenol molecule to produce phenol complexes **11a,b** followed by phenol proton abstraction by organic base (reactions 35, 36 and 21, 22—Table 2).

The complexation is very exothermic reaction even though unfavorable entropic effect increase these values in the case of Gibbs free energies. The complex formation increases acidity of phenol proton to such an extent that even such a weak base as DPP is able to abstract phenol proton to generate “controlled” radicals species **12a,b**. Both process the complex formation and the proton abstraction are more favorable for bidentate ligand which can easily be interpreted in terms of increasing electron density at Cu(II) center by third nitrogen thus decreasing its electronegativity. This hypothesis is proved by the fact that binding energies of Cu(I) phenol complexes **6a,b** are significantly less negative (reactions 33, 34—Table 2) and the proton abstraction is thermodynamically unfavorable (reactions 19, 20—Table 2). The proton abstraction from free phenol is even more unfavorable (reaction 18—Table 2) although solvation favors this process. The calculation results are in line with the mechanism proposal made by authors¹¹ where the reaction between Cu(II) and phenol is one of the ways to generate “controlled”

Scheme 3. Hydrogen Transfer in the Reaction of Oxidative Polymerization of Phenol^a



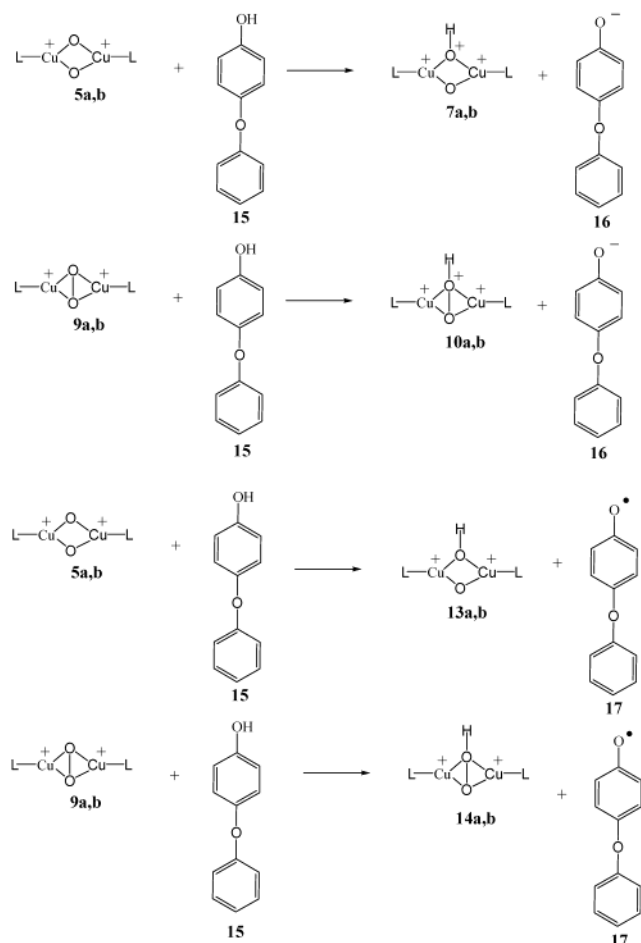
^a Formation and isomerization of μ - η^2 : η^2 -peroxodicopper(II) complexes. Key: **(a)** L = N,N,N',N'-tetramethylethylenediamine; **(b)** L = 1,4,7-trimethyl-1,4,7-triazacyclononane. Formation of mononuclear Cu(I) and Cu(II) complexes.

ment with experimental data. As seen, tridentate ligand increases the stability of (μ -oxo)dicopper(III) complex compared to bidentate one, slightly increasing the activation energy of isomerization. The relative stabilization of (μ -oxo)dicopper(III) complex with tridentate ligand is due to additional electrons providing by third nitrogen stabilizing highly electron deficient Cu(III) center. On the other hand, the more rigid structure of tridentate ligand slightly increases the activation energy of isomerization.

According to the mechanism for generation of “controlled” radicals proposed in ref 11, the “nucleophilic” complexes **1** (Scheme 1) are responsible for this process, while the “electrophilic” complex **4** generates “free” phenoxy radicals. The results of calculations show that is not the case. The first step of this mechanism is the phenol proton abstraction by μ - η^2 : η^2 -peroxodicopper(II) complexes (**9a,b**) (reactions 3, 8—Table 2). As can be seen, these reactions are highly endothermic. Even when the solvation is taken into account, the reaction energies are still highly positive, being well above 100 kcal/mol for both cases. The complex formation between phenol and copper(I) amine complexes (reactions 33, 34)

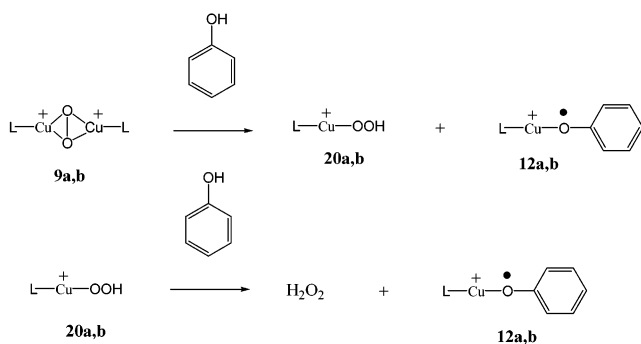
$\mu\text{-}\eta^2\text{:}\eta^2\text{-Peroxodicopper(II) (9a,b)}$ and $(\mu\text{-oxo})\text{dicopper(III) (5a,b)}$ complexes are almost isoenergetic, and the transformation of one to the other shows low activation energies (reactions 23, 24—Table 2) implying fast and reversible interconversion between isomers in agree-

Scheme 4. Proton and Hydrogen Transfer from 4-Phenoxyphenol to (μ -Oxo)dicopper(III) and μ - η^2 : η^2 -Peroxodicopper(II) Complexes^a



^a Key: (a) L = *N,N,N',N'*-tetramethylethylenediamine; (b) L = 1,4,7-trimethyl-1,4,7-triazacyclononane.

Scheme 5. Generation of "Controlled" Radicals 12a,b Starting from μ - η^2 : η^2 -Peroxodicopper(II) Complexes^a



^a Key: (a) L = *N,N,N',N'*-tetramethylethylenediamine; (b) L = 1,4,7-trimethyl-1,4,7-triazacyclononane.

increases the acidity of phenol hydrogen as seen from Table 2 (reactions 4 and 9); however, this is not enough to make the proton abstraction possible. The reaction energies are still too positive (79 and 86 kcal/mol when solvation is taken into account). A similar reaction with (μ -oxo)dicopper(III) complexes (**5a,b**) is also strongly endothermic (reactions 1, 2, 6,7), however less endothermic compared to μ - η^2 : η^2 -peroxodicopper(II) complexes (**9a,b**). This fact is definitely due to the difference in formal oxidation state of oxygen atoms in **5a,b** and **9a,b** complexes. While oxygen has a formal oxidation

Table 2. Gas and Solution Phase Reaction Energetics (kcal/mol) Calculated at GGAI/LACVP* Level of Theory

reaction	gas phase	solution (toluene)
1. 5a + PhOH = 7a + PhO ⁻	267.9	133.5
2. 5a + 6a = 7a + 8a	158.0	75.0
3. 9a + PhOH = 10a + PhO ⁻	286.8	156.3
4. 9a + 6a = 10a + 8a	177.8	79.1
6. 5b + PhOH = 7b + PhO ⁻	243.6	116.1
7. 5b + 6b = 7b + 8b	142.3	66.4
8. 9b + PhOH = 10b + PhO ⁻	261.6	135.3
9. 9b + 6b = 10b + 8b	160.4	86.2
10. 5a + PhOH = 13a + PhO [•]	1.6	1.4
11. 5a + 6a = 14a + 12a	-21.0	-20.0
12. 9a + PhOH = 14a + PhO [•]	26.2	27.0
13. 9a + 6a = 14a + 12a	3.7	5.0
14. 5b + PhOH = 13b + PhO [•]	-1.4	-1.8
15. 5b + 6b = 13b + 12b	-24.7	-24.5
16. 9b + PhOH = 14b + PhO [•]	24.1	23.0
17. 9b + 6b = 14b + 12b	0.8	0.3
18. DPP + PhOH = DPP ⁺ + PhO ⁻	115	59.3
19. DPP + 6a = DPP ⁺ + 8a	5.9	1.6
20. DPP + 6b = DPP ⁺ + 8b	13.6	10
21. DPP + 11a = DPP ⁺ + 12a	-105.1	-59.4
22. DPP + 11b = DPP ⁺ + 12b	-91.7	-49.3
23. 9a = 5a	4.9 (5.2) ^a	4.1 (4.7) ^a
24. 9b = 5b	1.5 (8.1) ^a	-0.4 (7.3) ^a
25. 5a + 15 = 7a + 16	266.0	137.3
26. 5b + 15 = 7b + 16	243.0	120.7
27. 9a + 15 = 10a + 16	285.0	160.2
28. 9b + 15 = 10b + 16	260.9	140.6
29. 5a + 15 = 13a + 17	2.5	2.9
30. 5b + 15 = 13b + 17	2.9	3.1
31. 9a + 15 = 14a + 17	27.1	27.8
32. 9b + 15 = 14b + 17	25.0	24.5
33. 18a + PhOH = 6a	-27.7 (-14.8) ^b	-21.7 (-8.2) ^b
34. 18b + PhOH = 6b	-22.7 (-9.2) ^b	-17.8 (-4.2) ^b
35. 19a + PhOH = 11a	-62.9(-48.2) ^b	-48.2(-24.1) ^b
36. 19b + PhOH = 11b	-49.8(-27.3)	-27.3 (-10.7) ^b
37. 9a + PhOH = 20a + 12a	-34.2	-7.2
38. 9b + PhOH = 20b + 12b	-33	-6
39. 20a + PhOH = 12a + H ₂ O ₂	-7.1	-3.5
40. 20b + PhOH = 12b + H ₂ O ₂	-1.8	-0.2
39 (41). 2(18a) + O ₂ = 9a	-20.1 (7.2) ^b	-44.6 (-17.3) ^b
40 (42). 2(18b) + O ₂ = 9b	-18.2 (6.3) ^b	-41.6 (-17.1) ^b

^a Activation energies. ^b Gibbs free energies.

state of -2 in complexes **5a,b**, the oxidation state of oxygen atoms in complexes **9a,b** is -1, making them less basic.

Another possibility is the hydrogen abstraction producing "free" phenoxy radicals (reactions 10, 14, 12, and 16 and Scheme 3). This reaction is not desirable since it decreases regioselectivity of oxidative polymerization process. As seen, the hydrogen abstraction is much more favorable compared to proton abstraction although not favorable enough to take place except for complex **5b** showing slightly negative reaction energies of -1.4 and -1.8 kcal/mol for gas phase and solution, respectively.

These data show that both (μ -oxo)dicopper(III) complexes (**5a,b**) and μ - η^2 : η^2 -peroxodicopper(II) complexes (**9a,b**) are oxidants by nature with complexes **5a,b** being the strongest oxidant as can be expected from higher oxidation level of Cu atoms in these complexes.

There is apparent contradiction in the behavior of **5a,b** complexes being better base and oxidant at the same time compared to **9a,b** complexes. Figure 1 shows optimized geometries of **5b** and **9b** molecules with calculated natural charges at Cu and oxygen atoms. As can be seen from Figure 1, the isomerization from μ - η^2 : η^2 -peroxodicopper(II) to (μ -oxo)dicopper(III) complex leads to perceptible electron density redistribution in the molecule.

The electron density moves from Cu centers to oxygen atoms on isomerization. This makes oxygen atoms in

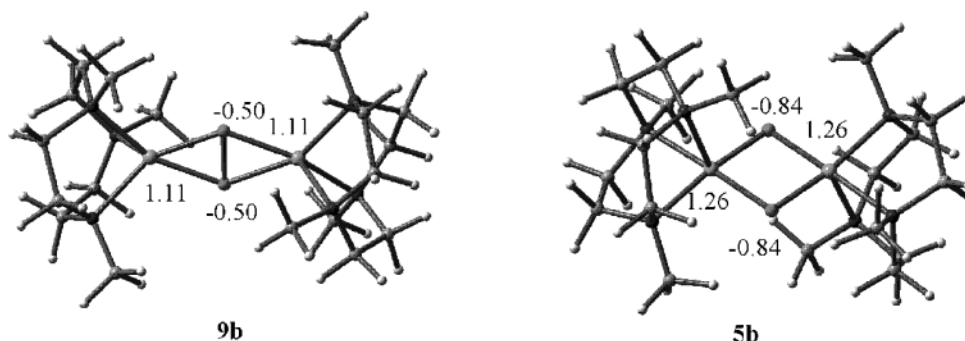


Figure 1. Optimized geometries and NPA charges for **5b** and **9b** molecules at the GGAI/LACVP* level of theory.

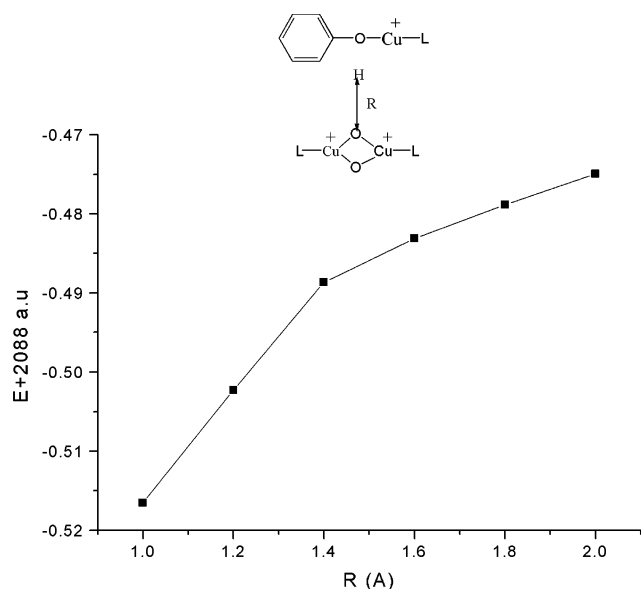


Figure 2. Results of potential energy scan for hydrogen transfer from **6b** to **5b** molecule at the GGAI/LACVP* level of theory.

5a,b complexes more basic compared to **9a,b** ones, thus favoring the proton transfer. On the other hand, the hydrogen transfer represents the oxidation of phenol oxygen, and (μ -oxo)dicopper(III) complex is a stronger oxidant compared to μ - η^2 : η^2 -peroxodicopper(II) as followed from lower lying LUMO (-0.36900 au for **5b**) compared to -0.35247 au for **9b**.

The hydrogen transfer facilitates the process greatly if one consider the reaction of Cu(I)–phenol complexes (**6a,b**) and not free phenols. These complexes easily form in the reaction mixture in the presence of the copper(I) amine complex and phenol (reactions 33, 34–Table 2). The hydrogen abstraction from complexes **6a,b** leads directly to the formation of “controlled” radicals **12a,b** (reactions 11, 13, 15, and 17). The reactions are exothermic for (μ -oxo)dicopper(III) complexes **5a,b** and endothermic for μ - η^2 : η^2 -peroxodicopper(II) complexes **9a,b**, thus showing an important new pathway for generation of “controlled” radical species involving (μ -oxo)dicopper(III) complexes. Solvation apparently does not affect the reaction energetics. All efforts to localize the transition state for the hydrogen transfer failed, showing that the activation energy for this process is essentially zero. Figure 2 shows the potential energy scan results for reaction 11 (Table 2).

As can be seen from the Figure 2 hydrogen transfer from complexes **6a,b** to (μ -oxo)dicopper(III) complexes **5a,b** shows no activation energies, and it is very easy

for it to occur under the reaction conditions of oxidative polymerization. It seems (μ -oxo)dicopper(III) complexes play very important roles in the generation of “controlled” radicals.

To test whether the energetics of proton and hydrogen transfer depends on the length of polymer chain, additional calculations have been carried out with 4-phenoxyphenol instead of phenol (Scheme 4). The results are listed in Table 2 (reactions 25–32).

As seen from Table 2, the energies of proton and hydrogen transfer from 4-phenoxyphenol to (μ -oxo)dicopper(III) and μ - η^2 : η^2 -peroxodicopper(II) complexes are quite similar (within 2 kcal/mol) to these for phenol suggesting that the proposed mechanism for generating “controlled” radicals is valid not only at the initial stages of polymerization but also at later polymerization steps as well.

Although the phenol proton abstraction is a very unfavorable reaction for μ - η^2 : η^2 -peroxodicopper(II) complexes, the overall process leading to the generation of “controlled” radicals **12a,b** is quite possible thermodynamically (reactions 37–40–Table 2, Scheme 5). Solvation affects greatly the reaction energetics making this process less favorable due to strong solvation of **9a** and **9b** dications. The question whether this process makes an important contribution to the generation of “controlled” radicals is related to the activation energy of these reactions. Since there is a fast and reversible interconversion between (μ -oxo)dicopper(III) and μ - η^2 : η^2 -peroxodicopper(II) complexes, reactions 37–40 will contribute significantly to the generation of “controlled” radicals only if their activation energies are comparable or lower than the activation energy of isomerization, 5–7 kcal/mol. Otherwise, the phenol hydrogen abstraction from complexes **6a,b** by (μ -oxo)dicopper(III) complexes (reactions 11, 15) will be the predominant reactions to produce “controlled” radical species. Consider that reactions 37–40 starting with the proton transfer can hardly compete with reactions 11 and 15.

Conclusions

A detailed quantum mechanical study for the generation of “controlled” radical species participating in regioselective polymerization of phenol has been carried out. According to calculations there are two pathways for generation of “controlled” radicals **12a,b**. One of them is the proton abstraction from phenol–Cu(II) complexes **11a,b** by organic base present in the reaction mixture while the other is related to the hydrogen abstraction of (μ -oxo)dicopper(III) complexes (**5a,b**) from Cu(I)–phenol complexes **6a,b**. μ - η^2 : η^2 -Peroxodicopper(II) complexes (**9a,b**) are too weak bases and oxidants to abstract either proton or hydrogen from phenol or

Cu(I)–phenol complexes. It seems it is (μ -oxo)dicopper-(III) complexes which are responsible for “radical controlled” oxidative polymerization of phenol.

Acknowledgment. This work was supported by a grant from DGAPA under Contract IN100902.

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MA0342731