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Ab Initio Calculation on the Reaction Mechanism of “Radical-Controlled” Oxidative Polymerization of Phenols

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Ab initio calculation on the reaction mechanism of “radical-controlled” oxidative polymerization (RCOP) of phenol catalyzed by μ-η^2:η^2-peroxo dicopper(II) complex (**1**) was performed. The key step is the reaction of **1** with phenol, for which two reaction routes have been postulated. One is through phenoxo copper(II) intermediate (route **X**), and the other is via the abstraction of hydrogen atoms from phenol (route **Y**). All structures of the possible intermediates in both routes were optimized, and the energy profiles of these routes were compared with each other. For the reaction of **1** with phenol, route **X** would be favored more than route **Y** based on the present calculation results and previous experimental data. In comparison, the reaction of **1** with 2,4-di-*t*-butylphenol, which has a bulky substituent at the *o*-position, was evaluated in a similar manner. Route **X** may also be possible in this reaction.

It has been very difficult to control the regioselectivity of oxidative polymerization of 2- and/or 6-unsubstituted phenols using conventional oxidation catalysts.[1,2] Recently, we have achieved “radical-controlled” oxidative polymerization (RCOP) of such phenols having at least one open *o*-position,[2–9] for example phenol (PhOH),[9] using a (1,4,7-triisopropyl-1,4,7-triazacyclononane)copper(II) (Cu(L^R): R = isopropyl (*i*Pr)) complex catalyst under dioxygen at 40 °C to give structure-regulated poly(1,4-phenylene oxide)s. The reaction mechanism is postulated as follows (route **X** in Scheme 1), in which the dimerization of PhOH is illustrated. μ-η^2:η^2-Peroxo dicopper(II) complex **1**[10,11] is exclusively formed as the active oxygen complex under the reaction conditions (stage **A**) and reacts with PhOH to give phenoxo copper(II) complex **2** and hydroperoxo copper(II) complex **3** (stage **B**). Reaction of complex **3** with PhOH gives **2** and hydrogen peroxide (stage **C**). Intermediate **2** is equivalent to phenoxyl radical copper(I) complex, which is not a free radical but a controlled radical, and hence, regioselective coupling from two molecules of **2** takes place to produce 4-phenoxyphenol (PPL, coupling product) and copper(I) complex **4** (stage **D**).

On the other hand, Tolman et al. reported that the same μ-η^2:η^2-peroxo dicopper(II) complex **1** liganded by L^{iPr} reacted with 2,4-di-*t*-butylphenol ($t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3\mathrm{OH}$) in the absence of dioxygen to give 3,3′,5,5′-tetra-*t*-butylbiphenyl-2,2′-diol (TBD) and bis(μ-hydroxo) dicopper(II) complex **5**.[12] Their kinetic study showed that **1** abstracted hydrogen atoms from the isopropyl group of the ligands in an intramolecular manner, suggesting another possible mechanism (route **Y** in Scheme 2). The intermolecular hydrogen abstraction of **1** from $t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3\mathrm{OH}$ gives **5** and 2,4-di-*t*-butylphenoxyl radicals (stage **E**), followed by the coupling of two molecules of the phenoxyl radical to produce TBD (stage **F**).

In this work, we evaluated both of the possible reaction routes **X** and **Y** in the reaction of μ-η^2:η^2-peroxo dicopper(II) complex **1** with PhOH and $t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3\mathrm{OH}$, respectively, by means of ab initio molecular orbital calculations. All the structures of the copper complexes and phenol derivatives in Schemes 1 and 2 were optimized, and the energy profiles of routes **X** and **Y** were compared with each other. As to the copper moiety, the ab initio calculations of the actual core Cu(L^{iPr}) were performed for the first time, although Cu(L^H) was previously reported to be calculated as a model of Cu(L^{iPr}).[13]

Calculation

Ab initio molecular orbital calculations were performed using the Gaussian 94[14] and Gaussian 98W[15] programs. Optimized geometries of copper complexes and phenol derivatives were obtained at Hartree–Fock (HF) level with STO-3G* basis function.[16,17] HF/6-31G* method was used to calculate of energies at the optimized structures.[18,19]

Results and Discussion

Optimized Structures of Cu Complexes. The structure-optimized Cu(L^R) (R = H and *i*Pr) complexes are as follows: μ-η^2:η^2-peroxo dicopper(II) complexes (**1a** and **1b**, respectively), phenoxo copper(II) complexes (**2a** and **2b**, respectively), 2,4-di-*t*-butylphenoxo copper(II) complexes (**2c** and **2d**, respectively), hydroperoxo copper(II) complexes (**3a** and **3b**, respectively), copper(I) complexes (**4a** and **4b**, respectively), and bis(μ-hydroxo) dicopper(II) complexes (**5a** and **5b**, respectively). The typical bond distances and angles of the optimized

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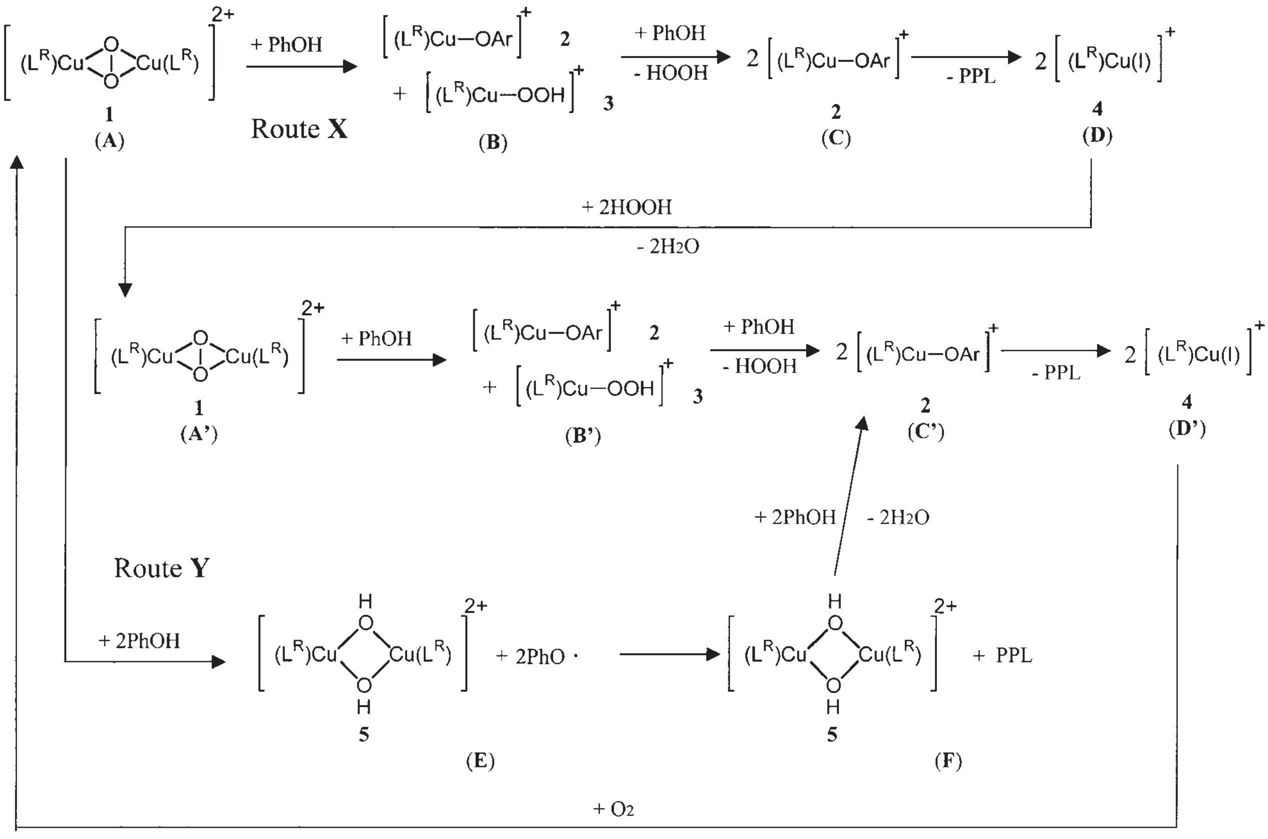
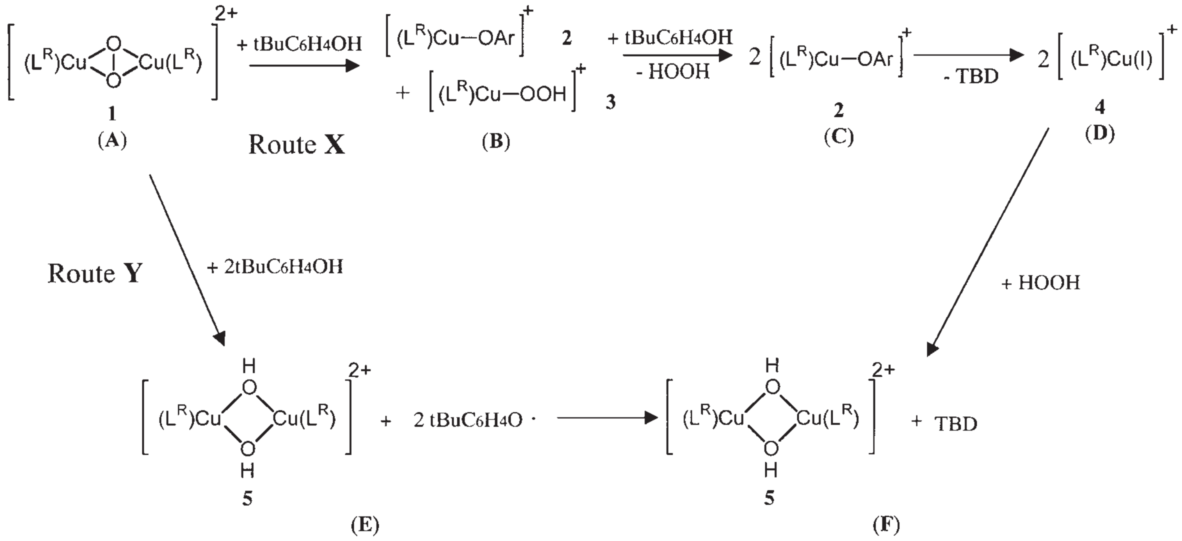


Scheme 1.



Scheme 2.

structures of these copper complexes are shown in Table 1.

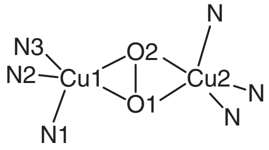
μ-η^2:η^2-Peroxo dicopper(II) complexes (**1a** and **1b**) possessed two distorted square-pyramidal CuN_3O_2 cores, in which Cu_2O_2 cores were formed as a diamond. The structures hardly differed from each other, and were almost the same as that of the μ-η^2:η^2-peroxo dicopper(II) complex with hydrotris(3,5-diisopropyl-1-pyrazolyl)borate (tpzb) ligand as determined by X-ray crystallography.[10]

Phenoxo copper(II) complexes (**2a** and **2b**) and 2,4-di-*t*-butylphenoxo copper(II) complexes (**2c** and **2d**) consisted of trigonal-pyramidal CuN_3O cores. The Cu–O distances of **2a**, **2b**, and **2c** (1.72–1.75 Å) were nearly equal to that of the structurally characterized 4-fluorophenoxo copper(II) complex with tpzb ligand (~1.73 Å),[20] however, the Cu–O bond of **2d** (~1.99 Å) was considerably longer than those of **2a**, **2b**, and **2c**, which is due to the steric repulsion of the three isopropyl substituents on the triazacyclononane ligand towards the two *t*-butyl substituents on the phenoxo moiety. Therefore, the actual copper complexes should be selected in the evaluation for the reaction via **2d**.

Table 1. Typical Bond Distances and Angles of Optimized Copper Complexes

Copper complexes		Typical bond distances/angstrom							Typical bond angles/degree		
μ-η^2:η^2-peroxo dicopper(II) complex		Cu–Cu	O–O	Cu–O1	Cu–O2	Cu1–N1	Cu1–N2	Cu1–N3	O1–Cu1–N1	O1–Cu1–N2	O1–Cu1–N3
$[(L^{H})_2Cu_2O_2]^{2+}$	**1a**	3.658	1.342	1.948	1.948	2.111	2.020	2.021	114.6	112.7	149.9
$[(L^{iPr})_2Cu_2O_2]^{2+}$	**1b**	3.724	1.333	1.969	1.986	2.123	2.085	2.063	103.6	110.8	155.0
$[(tpzb)_2Cu_2O_2]^{a,b)}$		3.560	1.412	1.903	1.927	2.258	2.000	1.993	114.2	107.2	150.4
phenoxo copper(II) complex					Cu–O	Cu–N1	Cu–N2	Cu–N3	O–Cu–N1	O–Cu–N2	O–Cu–N3
$[(L^{H})Cu(OPh)]^{+}$	**2a**				1.728	2.081	2.010	2.071	109.9	148.4	123.1
$[(L^{iPr})Cu(OPh)]^{+}$	**2b**				1.746	2.115	2.040	2.047	112.2	141.1	123.3
$[(L^{H})Cu(OC_6H_3tBu_2)]^{+}$	**2c**				1.722	2.086	2.018	2.070	110.4	147.2	124.2
$[(L^{iPr})Cu(OC_6H_3tBu_2)]^{+}$	**2d**				1.989	2.100	2.121	2.097	123.4	129.7	125.5
$[(tpzb)CuOC_6H_4F]^{a,c)}$					1.731	2.043	1.955	2.023	120.1	129.8	121.1
peroxo copper(II) complex					Cu–O	Cu–N1	Cu–N2	Cu–N3	O–Cu–N1	O–Cu–N2	O–Cu–N3
$[(L^{H})Cu(OOH)]^{+}$	**3a**				2.015	2.059	2.070	2.092	126.5	128.7	127.9
$[(L^{iPr})Cu(OOH)]^{+}$	**3b**				2.043	2.092	2.071	2.107	126.7	127.2	122.9
$[(tpzb)Cu(OOCm)]^{+\ a,d)}$					1.816	1.982	1.949	2.161	122.2	140.3	107.8
copper(I) complex						Cu–N1	Cu–N2	Cu–N3	N1–Cu–N2	N2–Cu–N3	N3–Cu–N1
$[(L^{H})Cu]^{+}$	**4a**					2.064	2.045	2.025	85.8	91.2	90.6
$[(L^{iPr})Cu]^{+}$	**4b**					2.075	2.047	2.033	89.9	94.0	93.5
$[(tpzb)Cu(CO)]^{a,e)}$						2.070	2.058	2.067	91.4	93.5	92.7
bis(μ-hydroxo) dicopper(II) complex		Cu–Cu	O–O	Cu1–O1	Cu1–O2	Cu2–O1	Cu2–O2		O1–Cu1–O2	O1–Cu2–N2	
$[(L^{H})_2Cu_2(OH)_2]^{2+}$	**5a**	3.058	2.414	1.791	1.796	2.136	2.124		84.6	69.0	
$[(L^{iPr})_2Cu_2(OH)_2]^{2+}$	**5b**	3.221	2.195	1.807	1.786	2.092	2.122		75.3	62.8	
$[(L')_2Cu_2(OH)_2]^{2+\ a,f)}$		3.009	2.445	1.922	1.951	1.930	1.951		78.3		

a) X-ray crystallography data. b) Ref. 11, tpzb = hydrotris(3,5-diisopropyl-1-pyrazolyl) borate. c) Ref. 20, OC_6H_4F = 4-fluorophenoxide. d) Ref. 21, OOCm=1-methy-1-phenylethyl-peroxide. e) Ref. 23. f) Ref. 24, L′=1,4-diisopropyl-1,4,7-triazacyclononane.



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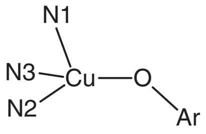

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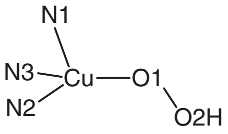

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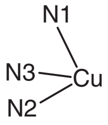

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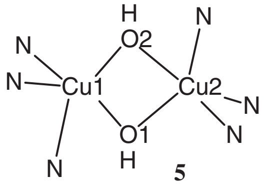

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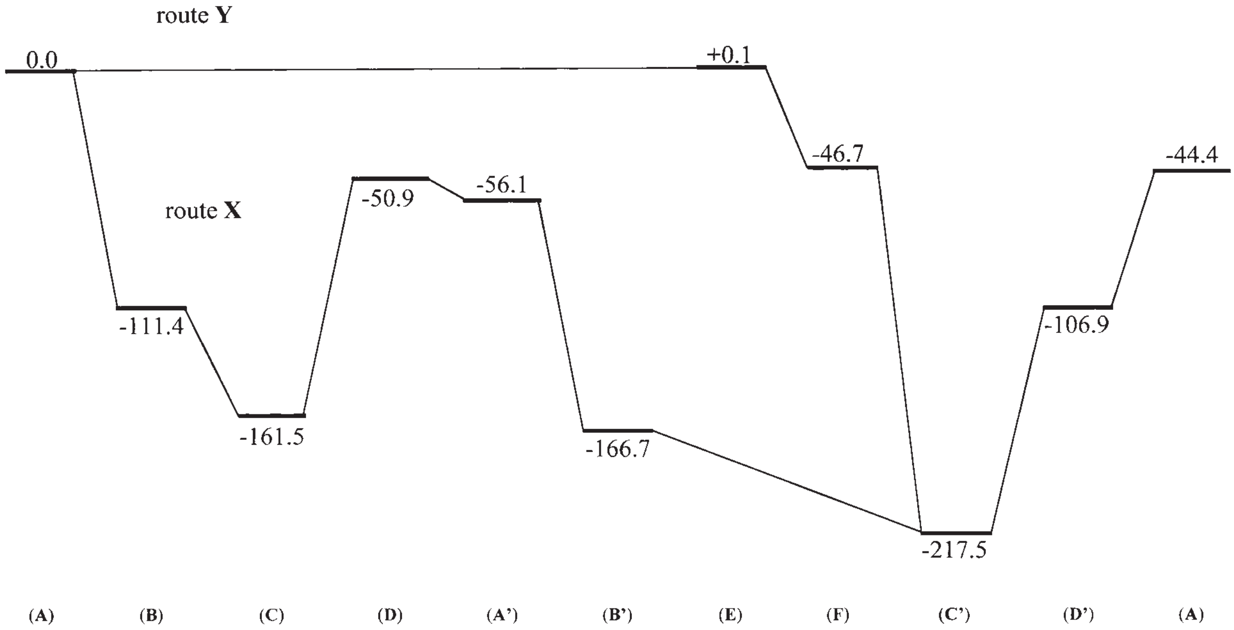


Fig. 1. Energy profiles (kcal/mol) for the reaction of **1b** with PhOH.

For hydroperoxo copper(II) complexes, changes in structure between **3a** and **3b** were hardly observed, and these structures were similar to that of a 1-methyl-1-phenylethylperoxo copper (II) complex with tpzb.[21,22] Copper(I) complexes (**4a** and **4b**) had a structure very similar to a (tpzb)Cu(CO) complex.[23]

In bis(μ-hydroxo) dicopper(II) complexes (**5a** and **5b**), the Cu2–O distances (2.09–2.14 Å) were longer than the Cu1–O ones (1.79–1.81 Å). Except for this distortion of the Cu_2O_2 core, these complexes possessed almost the same structures as that of 1,4-diisopropyl-1,4,7-triazacyclononane (L′).[24]

Energy Profiles of Routes X and Y. The overall scheme of oxidative coupling of PhOH to give PPL using Cu(L^{iPr}) catalyst is as follows:

$$4PhOH + O_2 \rightarrow 2PPL + 2H_2O \quad (-44.4\ \text{kcal/mol}).$$

In order to compare route **X** with route **Y** on the basis of the overall scheme, route **X** is represented by **A–B–C–D–A′–B′–C′–D′–A** in Scheme 1, whereas route **Y** is represented by **A–E–F–C′–D′–A**. The energy profiles of routes **X** and **Y** are shown in Fig. 1. All stages have the identical elementary composition, and their energy levels are based on the initial stage **A** (0.0 kcal/mol).

In the case of route **X**, the first step from stage **A** to stage **B** (−111.4 kcal/mol) is a very exothermic reaction, where μ-η^2:η^2-peroxo dicopper(II) complex **1b** reacts with one molecule of PhOH to give phenoxo copper(II) complex **2b** and hydroperoxo copper complex **3b**. This would be due to the acid–base reaction, in which PhOH acts as a weak acid (pK_a of PhOH = 9.9[25]) and O_2^{2-} as a strong base (pK_a of HO_2^- is not known, but should be much larger than 11.6, that of H_2O_2[25]). In the step to stage **C** (−161.5 kcal/mol), the reaction of **3b** with another molecule of PhOH to afford **2b** and H_2O_2 is also exothermic. The heat value of the second step (**B** to **C**) is smaller than that of the first step (**A** to **B**), probably owing to the weaker basicity of HO_2^- than that of O_2^{2-}. The step to stage **D** (−50.9 kcal/mol), the coupling of controlled radical **2b**, is significantly endothermic. The step to stage **A′** (−56.1 kcal/mol), the reaction of **4b** with H_2O_2 to give **1b** and H_2O,[4] is slightly exothermic. The next path from stage **A′** to **D′** is similar to that from **A** to **D**. Finally, the reaction of **4b** with O_2 to regenerate **1b** (**D′** to **A**) completes the catalytic cycle.

For route **Y**, the first step from stage **A** to stage **E** (0.1 kcal/mol) is a slightly endothermic reaction, in which μ-η^2:η^2-peroxo dicopper(II) complex **1b** abstracts hydrogen atoms from PhOH to give bis(μ-hydroxo) dicopper(II) complex **5b** and PhO•. The step to stage **F** (−46.7 kcal/mol), the free radical coupling of PhO•, is appreciably exothermic. The step to stage **C′** (217.5 kcal/mol), in which the reaction of complex **5b** and PhOH gives complex **2b**, is very exothermic. The next path from **C′** to **A** is the same as that in route **X**.

These calculated data show that, in the path from **A** to **C′**, the intermediate stages (**B**, **C**, **D**, **A′**, and **B′**) in route **X** are more stable than those (**E** and **F**) in route **Y**. Therefore, for RCOP, route **X** would be thermodynamically preferred to route **Y**. In terms of kinetics, the rate determining step in oxidative polymerization of PhOH by Cu(L^{iPr}) catalyst would be the coupling step of **2b**, because the mononuclear copper(II) complex speculated to be **2b** was observed in the steady state by ESR analysis.[9] However, the step of **2b** coupling (**C′** to **D′**) is included in both routes **X** and **Y**, so which is more possible can not be determined from the kinetic data. On the other hand, none of the products of free radical coupling were detected in oxidative coupling of PPL via μ-η^2:η^2-peroxo dicopper(II) complex **1b**.[3,4] Since the free radical coupling step is not included in route **X** but included in route **Y**, route **X** would be more consistent with the experimental data.

In a similar way, the overall scheme of the reaction of **1b** with $tBu_2C_6H_3OH$ to yield **5b** and TBD is as follows:

$$\mathbf{1b} + 2\ tBu_2C_6H_3OH \rightarrow \mathbf{5b} + \text{TBD} \quad (-55.5\ \text{kcal/mol}).$$

The energy profiles for this reaction were obtained in routes **X** and **Y** (Fig. 2). In the reaction of **1b** with $tBu_2C_6H_3OH$ in the

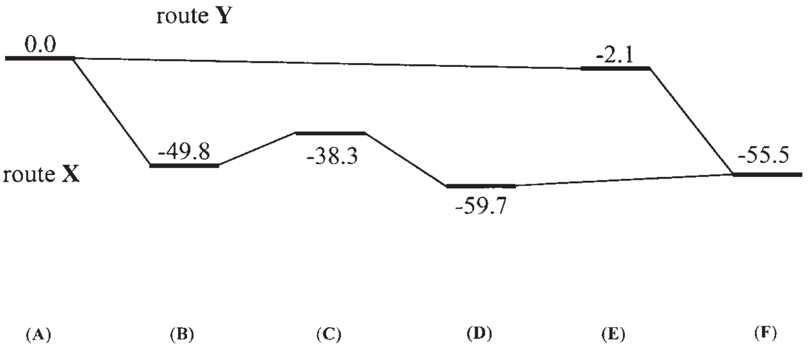
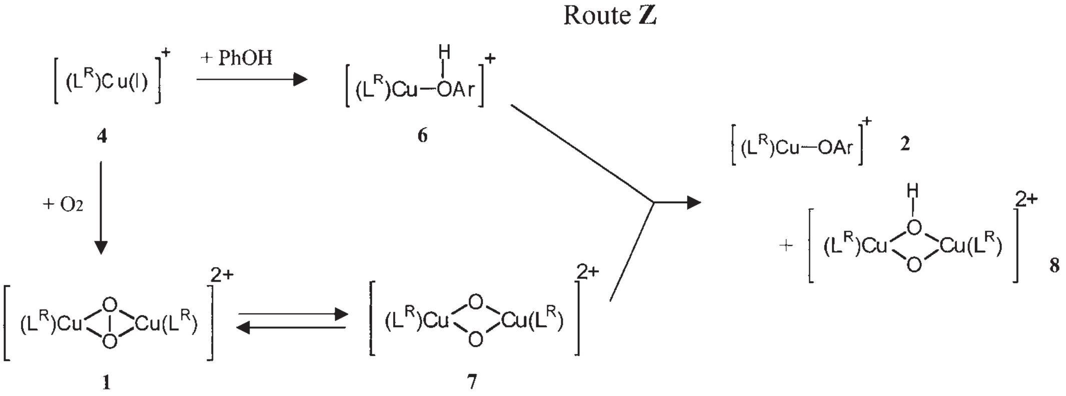


Fig. 2. Energy profiles (kcal/mol) for the reaction of **1b** with $t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3\mathrm{OH}$.



Scheme 3.

absence of dioxygen, the formation of **4b** was not detected and TBD was obtained exclusively, suggesting that two molecules of copper complex **4b** in stage **D** react with one molecule of H_2O_2 to produce one molecule of bis(μ-hydroxo) dicopper(II) complex **5b**. The energy profile of route **Y** is almost the same as that in Fig. 1. For route **X**, on the other hand, both stages **B** (−49.8 kcal/mol) and **C** (−38.3 kcal/mol) in Fig. 2 lie in an appreciably higher energy level than those in Fig. 1, since phenoxo copper(II) complex **2d** is less stable than **2b**, probably owing to the steric repulsion of **2d** (see above). However, the energies of **B**, **C**, and **D** in route **X** are lower than that of **E** in route **Y**. Therefore, route **X** may also be favored for the reaction of **1b** with $t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3\mathrm{OH}$.

Very recently, another route for RCOP has been proposed by ab initio calculation with a Cu(L^{Me}) model system (route **Z** in Scheme 3).[26] Copper(I) complex **4** reacts with PhOH to give phenol copper(I) complex **6**, a hydrogen atom of which is abstracted by bis(μ-oxo) dicopper(III) complex **7**, and equilibrated with μ-η^2:η^2-peroxo dicopper(II) complex **1** to form phenoxo copper(II) complex **2** with μ-hydroxo-μ-oxo dicopper(II,III) complex **8**. However, route **Z** is inconsistant with the difference in coupling selectivity in oxidative polymerization of PPL between **1** and **7**. That is, none of the free radical coupling products were detected for **1**, but considerable amounts of them were observed for **7**.[3,4]

Conclusions

The present calculation results and the previous experimental data indicate that the reaction of μ-η^2:η^2-peroxo dicopper(II) complex **1** with PhOH in RCOP would prefer the route through phenoxo copper(II) complex **2** to the route therough the abstraction of hydrogen atoms from PhOH. On the other hand, the route through **2** may also be favored for that with $t\mathrm{Bu}_2\mathrm{C}_6\mathrm{H}_3\mathrm{OH}$, which has a bulky substituent at the *o*-position. This study is the first example of structure-optimization of actual copper complexes with $L^{i\mathrm{Pr}}$ ligand using ab initio calculations, leading to the precious evaluation of stability of the reaction intermediates.

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