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Decomposition of alkyl hydroperoxide by a copper(I) complex: insights from density functional theory

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ABSTRACT

The B3LYP theory and scaled hypersphere search method are utilized to explore pathways of $(HO)_2PS_2Cu$-mediated CH_3OOH decomposition, a model reaction of alkyl hydroperoxide with cuprous dialkyldithiophosphate $[(RO)_2PS_2Cu]$. It is found that the decomposition of CH_3OOH mediated by the copper(I) complex may lead to formaldehyde and water molecules via O–O bond heterolysis and subsequent intramolecular hydrogen transfer, with retainment of the copper(I) complex. The subsequent hydrogen transfer event and formation of water may add new understanding to the $(RO)_2PS_2Cu$-mediated decomposition process of alkyl hydroperoxide. The oxygen transfer from CH_3OOH to $(HO)_2PS_2Cu$ moiety, as an O–O bond cleavage manner of CH_3OOH, is also found to occur.

1. Introduction

Decomposition of alkyl hydroperoxides (ROOH), which are usually accumulated via autoxidation of hydrocarbon or its derivatives, has attracted renewed interest because of its direct relevance to life science,[1] organic synthesis,[2,3] and industrial technology.[4] Due to the lability of RO–OH bond, ROOH can be readily decomposed by heat, light, or by reacting with other substances, such as base,[5–7] heteroatom nucleophiles,[8] metals,[4] or vitamin C.[9] Generally, the decomposition of ROOH occurs via either hydrogen abstraction or O–O bond cleavage including oxygen atom transfer event (reaction 1 in Scheme 1). The decomposition manner and resulting products depend on reaction conditions and interaction partner, and different mechanisms may be simultaneously followed.[4] The hitherto reported metal-mediated decomposition of ROOH occurs mainly via the O–O bond heterolysis leading to RO radical and OH anion[4] or O–O bond homolysis leading to RO and OH radicals (reactions 2 and 4 in Scheme 1).[10] There is an exception that the decomposition of ROOH occurs via hydrogen-atom transfer from metal hydroperoxide to oxo metal complex.[11] During the ROOH decomposition, the metal complex, if applied, is often destroyed by ROOH. In the heterolysis, the oxidized metal may attract the hydroxyl hydrogen atom of an additional ROOH (reaction 3 in Scheme 1). The resulting radicals were thought to undergo subsequent reactions, such as the radical-initiated autoxidation. For example, more than 30 years ago, Howard and co-workers[12] reported that the initial reaction of tertiary hydroperoxide with $[(RO)_2PS_2]_2Cu$ (cupric dialkyldithiophosphate) is a free radical chain process giving alkoxy radical via O–O bond heterolysis. The resulting alkoxy radical then abstracts a hydrogen from excess hydroperoxide to give alkylperoxy radical, and the copper (II) complex was converted to copper sulfate by reaction with the peroxy radical. About 10 years later, it was reported[13] that the reaction of $[(RO)_2PS_2]_4Cu_4$ with cumene hydroperoxide (a tertiary hydroperoxide) underwent the O–O bond cleavage and subsequent bond-arrangements mainly yielding phenol. In that work, the author also argued that the copper(I) complex formed a corresponding acid $(RO)_2PS_2H$ during the reaction, and it is this acid that is the catalyst for hydroperoxide decomposition. These works reflect that the reaction of alkyl hydroperoxides with such copper complexes is very complicated.

$$\mathrm{ROOH + RSR} \longrightarrow \mathrm{RS(O)R + ROH} \qquad (1)$$

$$\mathrm{ROOH} + \mathrm{M}^{+n} \longrightarrow \mathrm{RO}\bullet + \mathrm{OH}^{-} + \mathrm{M}^{+(n+1)} \qquad (2)$$

$$\mathrm{ROOH} + \mathrm{M}^{+(n+1)} \longrightarrow \mathrm{ROO}\bullet + \mathrm{H}^{+} + \mathrm{M}^{+n} \qquad (3)$$

$$\mathrm{ROOH} + \mathrm{M}^{+n} \longrightarrow \mathrm{RO}\bullet + \bullet\mathrm{OH} + \mathrm{M}^{+n} \qquad (4)$$

Scheme 1. Decomposition of alkyl hydroperoxide (M = metal).

It has been known for a long time that cuprous dialkyldithiophosphate $(RO)_2PS_2Cu$ can serve as an excellent antioxidant in lubricating oil by scavenging alkylperoxy radical and by decomposing alkyl hydroperoxides.[14–18] One of the authors also previously synthesized the $(RO)_2PS_2Cu$ complex and tested its antioxidation performance.[18] To the best of our knowledge, however, the

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decomposition pathway of alkyl hydroperoxides mediated by $(RO)_2PS_2Cu$ remains unreported both experimentally and theoretically possibly due to the complexity of the copper-mediated decomposition reaction and due to the difficulties in global modeling decomposition pathways. With the development of computational techniques, it is now possible to model certain chemical reactions, such as decomposition of alkyl hydroperoxides.[10,19] It also becomes possible to explore reaction potential energy surface (PES) both globally and automatically by a new technique developed in our group.[20–23] We had successfully explored the PES of isomerization reaction of $(RO)_2PS_2Cu$ and its reaction with alkylperoxy radical.[20] In this study, the reaction of CH_3OOH with $(HO)_2PS_2Cu$ is computed with a purpose of modeling the $(RO)_2PS_2Cu$-mediated decomposition process of alkyl hydroperoxide. Such modeling is on the basis of the result that alkyl group (R) of $(RO)_2PS_2Cu$ shows no significant effect on the reaction of $(RO)_2PS_2Cu$ with alkylperoxy radical,[20] and the RO groups are not actively involved in the reaction with CH_3OOH (vide infra). It is found that the $(HO)_2PS_2Cu$-mediated O–O bond heterolysis of CH_3OOH is easily followed by intramolecular hydrogen transfer leading to formaldehyde and water molecules, with retainment of the copper(I) complex. The pathway of oxygen atom transfer as a metal-mediated O–O bond cleavage manner is also found.

2. Computational method

During our study on the exploration of PES, we found that the scaled hypersphere search (SHS) method is quite efficient for global exploration of PES. The SHS method has been previously described in detail,[24–26] and is also utilized here for global exploration of the decomposition pathway. The calculations were performed at the B3LYP/BSII//B3LYP/BSI level. In the BSI, the LanL2DZ basis set and associated pseudopotential[27,28] were used for the Cu atom, and the 6-31+G** basis set was used for the remaining atoms. In the BSII, the 6-311+G* basis set containing f-polarization function was used for the Cu atom and the 6-311+G** basis set for the others. The analytic frequency calculations were performed at the B3LYP/BSI level to verify the minima and TSs and to get the thermodynamic data. The stability of wave function was tested. The IRC followings have been performed during the SHS calculations. Such methodological strategy was previously assessed for similar system and got satisfactory results.[20] Except for the SHS procedures, all the calculations were carried out utilizing GAUSSION 03 program.[29]

3. Results and discussion

The computed free-energy profile and optimized stationary points are shown in Figures 1 and 2, respectively. In Figure 1, the electronic energies are also included for estimation of entropy effect. As seen from this figure, the prereaction complex **1** is lower in free energy by 5.1 kcal/mol compared to isolated $(HO)_2PS_2Cu$ and CH_3OOH reactants. In the **1**, the methyl hydroperoxide coordinates to Cu atom via its hydroxyl oxygen atom. The **1** feasibly undergoes a S–Cu bond cleavage leading to **2**. This transformation occurs via a transition state, **TS[1–2]**, with a free-energy barrier of 4.2 kcal/mol. The S1···Cu distance of 3.16 Å in the **2** (Fig. 2) is significantly longer than the sum of covalent atomic radii of Cu (1.38 Å) and S (1.02 Å) atoms, suggesting no covalent interaction between the S1 and Cu atoms in **2**. The **2** goes through **TS[2–3]** leading to an isomeric structure **3**. The free energy shows that the **3** is slightly lower than the **2** by 0.7 kcal/mol. A close look at the structures of the **2** and **3** indicates that the binding situation of CH_3OOH moiety is different. Such structural variation shortened the S1···Cu distance of **3** (2.76 Å, see Fig. 2) and may make **3** slightly more stable compared with **2**. The **3** further overcomes **TS[3–4]** with a free-energy barrier of 15.7 kcal/mol to give compound **4** via intramolecular concerted transfers of the hydroxyl oxygen atom (from CH_3OOH moiety to S1 atom) and hydrogen atom (from the hydroxyl oxygen to peroxy oxygen atom). Such intramolecular atom transfer event resulted in a five-membered ring structure and an alcohol moiety coordinating to the metal

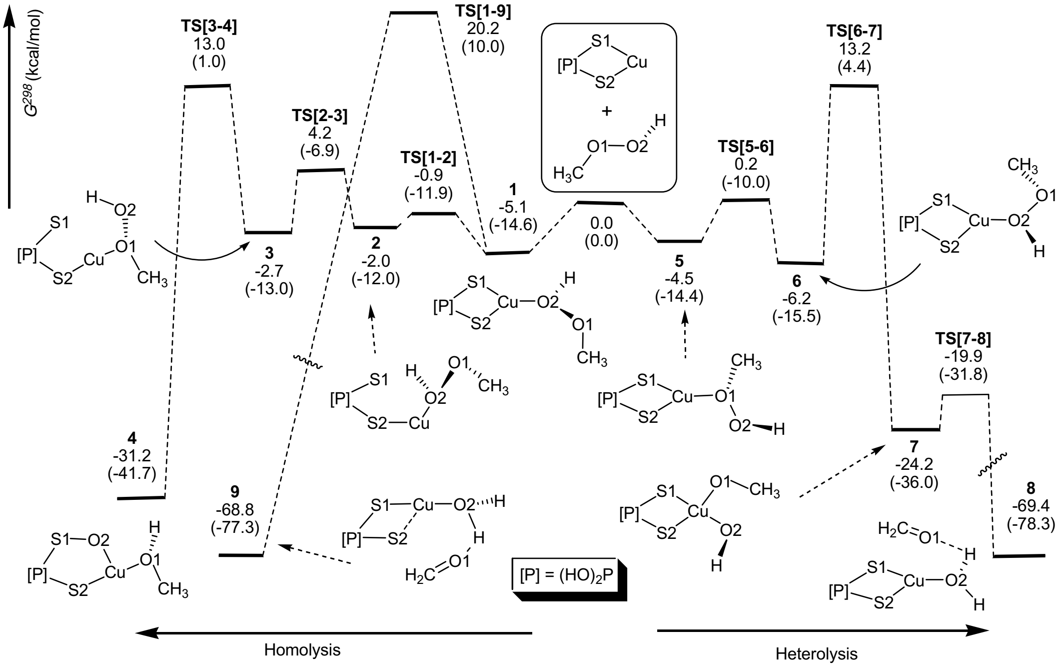
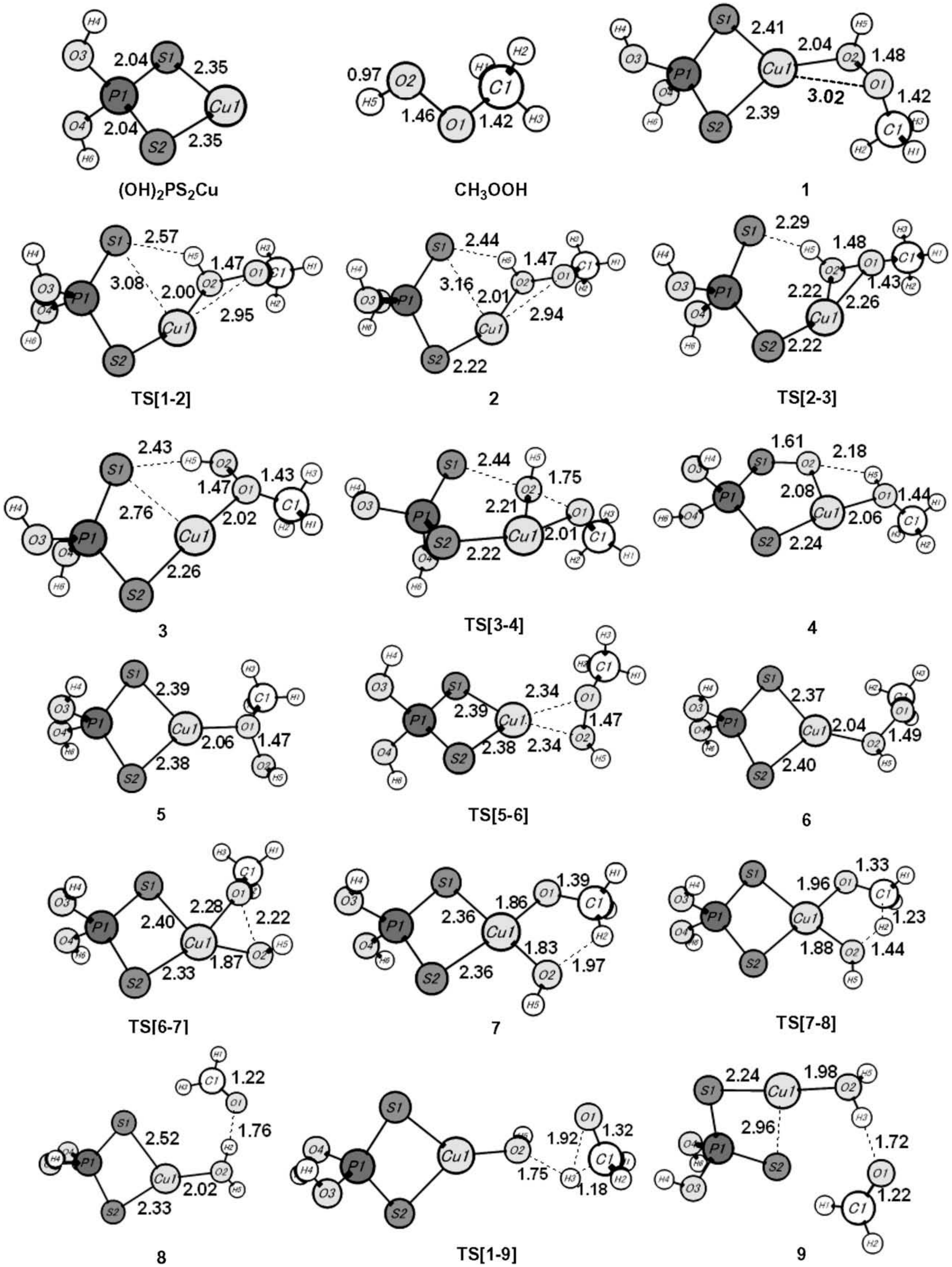


Figure 1. Computed free energy (G^{298}, 1 atm) profile for the $(HO)_2PS_2Cu$-mediated CH_3OOH decomposition. The free energy are obtained by adding zero-point energy and thermal corrections obtained by B3LYP/BSI calculation to the B3LYP/BSII energy, respectively. The electronic energies are included in the parentheses. The energies (in kcal/mol) are relative to isolated reactants, and the structures of minima are schematically shown.



$(OH)_2PS_2Cu$ CH_3OOH **1**

TS[1-2] **2** **TS[2-3]**

3 **TS[3-4]** **4**

5 **TS[5-6]** **6**

TS[6-7] **7** **TS[7-8]**

8 **TS[1-9]** **9**

Figure 2. Optimized stationary points (distances in Å).

center via its O atom (see structure **4** in Figs. 1 and 2). Alcohol products were also previously observed in the reaction system of tertiary alkyl hydroperoxide with copper complex.[12,13] An analysis of the imaginary mode of **TS[3–4]** indicates that such concerted atom transfers occur via the rotation of hydroxyl group of hydroperoxides, which are similar to decomposition manner mediated by metal-free organic sulfides.[19] A natural population analysis (NPA) indicates that the Cu atom carries charge of 0.70 in the bare $(HO)_2PS_2Cu$ and 0.76 in the **4**, suggesting that the net conversion of **1** to **4** takes place via the O–O bond homolysis without metal oxidation.

During the search for the decomposition pathway, complex **5** was also located (Fig. 1). The **5** shows the binding between Cu atom and the peroxide oxygen atom of CH_3OOH moiety, and is slightly higher in free energy by 0.6 kcal/mol than the **1** showing the interaction of Cu atom with the hydroxyl oxygen atom. The **5** may easily adopt more stable structure **6** via **TS[5–6]**, having a free-energy barrier of 4.7 kcal/mol. The **6** is actually similar to **1** but lower in free energy by 1.1 kcal/mol than the **1**. The optimized structures show that relative orientations of CH_3OOH moiety and the OH groups of $(HO)_2PS_2^-$ ligand in the **6** are different from those in the **1** (see Fig. 2). The small energy difference between **5** and **6** (less than 2.0 kcal/mol) and the low interconversion energy barrier (<6.5 kcal/mol) indicate the ease of such interconversion and suggest that both **5** and **6** may exist at initial reaction stage. Unlike the **1** undergoing O–O bond homolysis leading to **4**, the complex **6** may adopt heterolysis manner via **TS**[**6**–**7**] to give product **7** with the resulting OH anion and CH_3O radical, both of which coordinate to the metal atom (see structure **7** in Fig. 2). Such heterolysis feature is suggested by more charged Cu atom (1.18) of **7** compared with that (0.70) of $(HO)_2PS_2Cu$. This process has relative free-energy barrier of 19.4 kcal/mol and is exergonic by 24.2 kcal/mol relevant to isolated reactants. It is obviously that such decomposition of CH_3OOH follows the conventional metal-mediated heterolysis manner of alkyl hydroperoxides, which results in metal oxidation and formation of OH anion. Interestingly, the compound **7** may easily further undergo hydrogen transfer from the methyl group to the OH moiety to yield **8**, in which the resulting H_2O and CH_2O are connected via hydrogen bond, and the H_2O moiety coordinates to the metal atom (Fig. 2). The hydrogen transfer transition state, **TS[7–8]**, has rather low free energy (−19.9 kcal/mol) relevant to isolated reactants. The conversion of **7** to **8** is a low barrier (free-energy barrier of 4.3 kcal/mol) and significantly exergonic process (exergonic by 45.2 kcal/mol). The driving force of such hydrogen transfer could be the electron-rich character of the OH group binding to the Cu atom. To the best of our knowledge, it is reported here, for the first time, that metal-mediated decomposition of CH_3OOH may lead to H_2O and H_2CO via heterolysis O–O cleavage and subsequent intramolecular hydrogen-atom transfer. In theory, any primary hydroperoxide may follow such decomposition pathway finally leading to aldehyde and water. It is known that homolysis of ROOH may lead to free OH radical, which can abstract hydroxyl hydrogen atom of excess ROOH to produce water.[4] The current computation shows a dissociation pathway that leads to water via hydrogen transfer from methyl to the resulting OH moiety (see the formation of **8** in Fig. 1). This computational result provides theoretical evidence for an alternative pathway leading to water in the decomposition process of alkyl hydroperoxide. The rate-determining step for the formation of **8** could be the conversion of **6** to **7** via **TS**[**6**–**7**]. The relative free energies of **TS[6–7]** (13.2 kcal/mol) and **TS[3–4]** (13.0 kcal/mol) are similar at 298 K (Fig. 1). Considering that the average working temperature of lubricating oil in engine is 500 K, we also calculated the free energies of **TS[6–7]** and **TS[3**–**4]** at this temperature. It was found that the **TS[6–7]** is lower than **TS[3–4]** in free energy (500 K) by 2.5 kcal/mol. The similar relative free energies of these TSs suggest that the formations of **8** and **4** may be kinetically competitive. However, the significant exothermic feature indicates a thermodynamic preferability for formation of **8**. In view of the retainment of $(HO)_2PS_2Cu$ moiety in the product **8**, such process may serve as a model for future attempts in catalysis design.

Another possible decomposition pathway leading to H_2O and H_2CO moieties is from the **1** to **TS[1**–**9]** to **9** (Fig. 1). In the **9**, the S2–Cu contact of 2.96 Å (Fig. 2) suggests no covalent interaction between S2 and Cu atoms. This process occurs via concerted intramolecular α-H transfer and the O–O bond cleavage. Such concerted event is suggested by the displacement vector of the imaginary mode of **TS[1–9]**. Although the relative free energy of **TS**[**1**–**9**] is higher than that of **TS**[**6**–**7**] by 7.0 kcal/mol, the moderate relative free-energy barrier height (20.2 kcal/mol) for **TS[1–9]** and the significant exergonic character (exergonic by 68.8 kcal/mol) suggest the feasibility of the transformation from **1** to **9**. It is noteworthy that the **TS[1**–**9]** shows a three-coordinate hydrogen (H3) and a four-membered ring structure constructed by the H3, C1, O1 and O2 atoms (see structure of **TS[1–9]** in Fig. 2). Such structural features are suggested by the orbital isosurfaces of **TS**[**1**–**9**] (see Supplementary data). The HOMO − 6, HOMO − 11, and HOMO − 19 of **TS[1–9]** show the interactions between 1s orbital of the hydrogen and the 2p orbitals of the carbon and two oxygen atoms of the CH_3OOH moiety. The HOMO − 19 orbital also suggests a four-membered ring structure. Like the net transformation from **1** to **4**, the natural charge population on the Cu atom of **9** (0.68) is similar to that of $(HO)_2PS_2Cu$ (0.70), suggesting a homolysis event. In comparison with the conversion of **5** to **8**, the transformation from **1** to **9** offers same dissociation products but follows different mechanism. It was previously showed that the solvation of lubricating oil mainly composed of alkanes and has minor effect on the energies (decreased by less than 2.0 kcal/mol) for similar reaction because of nonpolarity of such alkane solvent.[20] It is expected that the solvation should not have significant effect on the energies reported here.

4. Conclusion

The decomposition of methyl hydroperoxide mediated by the copper(I) complex, $(HO)_2PS_2Cu$, has been computationally found to preferably occur via O–O bond heterolysis and subsequent intramolecular hydrogen transfer leading to water and formaldehyde molecules, with retainment of the copper(I) complex, or via an oxygen atom transfer leading to alcohol species, with destroyed copper(I) complex. The former dissociation manner may shed new light on the decomposition mechanism of alkyl hydroperoxide mediated by cuprous dialkyldithiophosphate $[(RO)_2PS_2Cu]$ and may serve as a model for future catalysis design. An alternative and less favorable process leading to water and formaldehyde is also found to occur via concerted intramolecular hydrogen transfer and the O–O bond cleavage. This work also shows that the scaled hypersphere search method is efficient to automatically explore pathways of certain reactions.

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Supplementary data

Supplementary data (figures and table give displacement vectors of imaginary mode of some important transition state, orbital isosurfaces of **TS**[**1**–**9**], and optimized Cartesian coordinates of stationary points) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.09.065.

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