

A Global Exploration of Dissociation Channel and Antioxidation Reaction Pathways of CuDDP by the Scaled Hypersphere Search Method

Department of Chemistry, Graduate School of Science, Tohoku University.

○Yi Luo, Satoshi Maeda, Koichi Ohno

【Introduction】 Lubricating oils in crankcase automotive engines are known to undergo oxidative degradation leading to products believed to be responsible for sludge deposits in used oils. Oil deterioration results in a loss of lubrication, with the signals shown by the appearance of sludge. Efforts aimed at reducing sludgy formation may extend the life span of the lubricant and prevent failure in service. Utilizing of additive, such as antioxidant to prevent oxidation and antiwear agent to protect the surface of engine parts, is a common strategy to reduce the formation of sludge. Obviously, knowledge about how these additives behavior is highly required for the development and usage of these additives. As an antiwear and antioxidation additive in lubricating oil, the cuprous dialkyldithiophosphorate (CuDDP, see Chart 1a) has been industrially applied for a long time. However, its isomerization and decomposition process as well as antioxidation mechanism are yet to be fully understood. In this connection, our group has successfully developed the scaled hypersphere search (SHS) method, which enables one to globally explore reaction pathways on the potential energy surface (PES). The SHS method has been utilized here to investigate the dissociation channels of CuDDP and its reaction with $\text{CH}_3\text{OO}\cdot$ radical.

【Method】 The SHS method is an uphill-walking technique to automatically explore reaction pathway from a given equilibrium structure (EQ).¹⁻³ Such an exploration of reaction pathway is executed by detecting anharmonic downward distortions (ADD) as a symptom of chemical reaction.¹⁻³ To effectively detect the ADD, a given-EQ-centered hypersphere surface is introduced in the SHS technique. Such a hypersphere surface is expanded by the scaled normal coordinates q_i , which can be defined by normal coordinates Q_i and the respective eigenvalues λ_i , viz. $q_i = \lambda_i^{1/2} Q_i$. During the reaction pathway following on the scaled hypersphere surface, the conventional optimization scheme and downhill-walking technique may be utilized. Such a pathway tracking may lead to transition states, dissociation channels, and new EQs. After the reaction pathways are traced for all of EQs via one-after-another manner, the global potential energy surface may be therefore figured. Such an SHS method has been successfully applied to main-group element compounds.⁴⁻⁶ In this work, we extended its application to transition-metal assisted chemical reactions. A model compound $(\text{HO})_2\text{S}_2\text{PCu}$ (Chart 1b) was used in the pathway explorations. The primary search for the pathways was performed at the B3LYP level of theory, with the combination of 6-31G basis set for C and H atoms, the 6-31G* for S and P atoms, and the LanL2DZ for Cu atom.

【Results and Discussion】 A global search for the dissociation channels of $(\text{OH})_2\text{PS}_2\text{Cu}$ suggests that two feasible dissociation reactions occur via the cleavages of a P–O bond and an H–O bond, respectively. However, its decomplexation leading to $(\text{HO})_2\text{PS}_2^-$ and Cu^+ is energetically unfavorable (see Scheme 1). Furthermore, the isomerizations of the $(\text{OH})_2\text{PS}_2\text{Cu}$ (Chart 1b) were found to involve various chemical bond rearrangements, which are kinetically feasible but endergonic. For example, the (H)O–Cu bond formation concerted with a S–Cu bond cleavage leading to an OH-bridging structure needs to overcome a free-energy barrier of 13.2 kcal/mol and is endergonic by 10.6 kcal/mol.

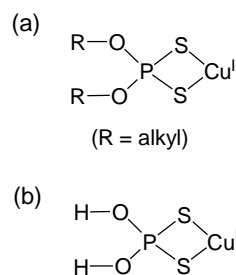
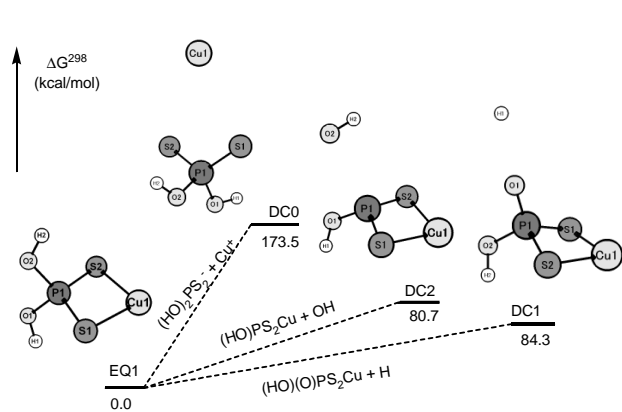
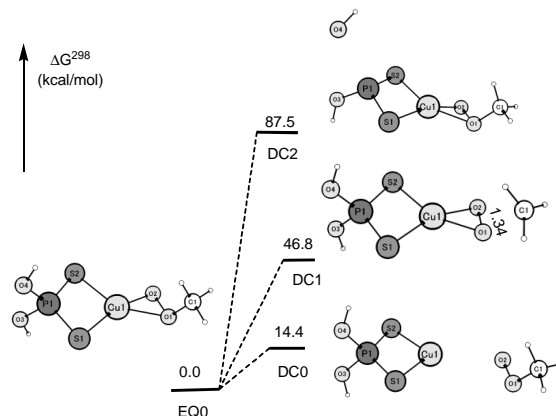


Chart 1. (a) The schematic representation of CuDDP and (b) and its model compound



Scheme 1. Dissociation channels of $(\text{OH})_2\text{PS}_2\text{Cu}$



Scheme 2. Dissociation channels of $(\text{OH})_2\text{PS}_2\text{Cu-OOCH}_3$ complex

To see whether the alkyl group of CuDDP has significant effect on the energy profile for such reactions, seven kinds of R substituents were considered for alkoxy-bridging isomerization reaction. These R substituents considered are propyl, *iso*-propyl, pentyl, *iso*-pentyl, octyl, *iso*-octyl and 2-methyl-octyl groups. The results showed that such isomerizations with energy barriers of 13-15 kcal/mol were endergonic by 11-13 kcal/mol, which are compared to those for the isomerization of model compound $(\text{OH})_2\text{PS}_2\text{Cu}$, respectively. This suggests that the alkyl group of CuDDP does not significantly affect the energy profile and the model compound used here is proper for PES exploration. Since the additives react at high temperatures under typical engine conditions, the temperature effect was also investigated for the dissociation reactions (Table 1). The average engine temperature is considered to be 500 K. The temperature up to 700 K was considered. For DC2 channel of in Scheme 1, the dissociation energy decreased with the increase of temperature investigated (Table 1). However, no significant effects on the dissociation energy for DC0 and DC1 channels possibly due to the resulting atomic species. The CuDDP-assisted decomposition of $\text{CH}_3\text{OO}\cdot$ was also investigated by the SHS method (Scheme 2). The $\text{CH}_3\text{OO}\cdot$ radical coordinates to $(\text{OH})_2\text{PS}_2\text{Cu}$ in two fashions, μ_1 and μ_2 , and the CuDDP- (μ_2) - OOCH_3 complex was computed to be less stable by 1.5 kcal/mol compared to CuDDP- (μ_1) - OOCH_3 at the B3LYP level of theory combined with LanL2DZ basis set for Cu and the 6-31+G** for the remained atoms. For CuDDP- (μ_2) - OOCH_3 complex, the de-complexation of $\text{CH}_3\text{OO}\cdot$ radical and the C–O bond cleavage are more favorable compared to the composition of $(\text{OH})_2\text{PS}_2^-$ anion ligand (Scheme 2). The EQ0 shown in Scheme 2 also easily undergoes O–O bond cleavage, which overcomes an energy barrier of 28.9 kcal/mol and is endergonic by 27.2 kcal/mol relative to EQ0. The dissociation energies of CuDDP- (μ_2) - OOCH_3 under various temperature are also included in Table 1. Like DC2 dissociation channel of $(\text{OH})_2\text{PS}_2\text{Cu}$, the dissociation of CuDDP- (μ_2) - OOCH_3 complex requires less energy under higher temperature, suggesting that the increase of temperature may accelerate CuDDP-assisted decomposition of alkylperoxy radical. This is in line with the fact that CuDDP is industrially applied as a high-temperature antioxidant.

Table 1. Dissociation free energies (kcal/mol) of $(\text{OH})_2\text{PS}_2\text{Cu}$ and CuDDP- (μ_2) - OOCH_3 under various temperatures (K)

Temperature	$(\text{OH})_2\text{PS}_2\text{Cu}$			CuDDP- (μ_2) - OOCH_3		
	DC0	DC1	DC2	DC0	DC1	DC2
300	173.6	84.3	80.6	14.3	46.7	87.3
400	174.7	84.5	76.7	10.6	43.1	83.3
500	176.1	84.8	72.7	7.1	39.4	79.3
600	177.5	85.1	68.7	3.6	35.8	75.3
700	179.1	85.4	64.8	0.1	32.1	71.3

[References] (1) Ohno, K.; Maeda, S. *Chem. Phys. Lett.* **2004**, *384*, 277. (2) Maeda, S.; Ohno, K. *J. Phys. Chem. A* **2005**, *109*, 5742. (3) Ohno, K.; Maeda, S. *J. Phys. Chem. A* **2006**, *110*, 8933. (4) Yang, X.; Maeda, S.; Ohno, K. *J. Phys. Chem. A* **2005**, *109*, 7319. (5) Yang, X.; Maeda, S.; Ohno, K. *Chem. Phys. Lett.* **2006**, *418*, 208. (6) Yang, X.; Maeda, S.; Ohno, K. *J. Phys. Chem. A* **2007**, *111*, 5099.