Computational Studies on the Effects of Substituents on the Structure and Property of Zinc Dialkyldithiophosphates

Weiguo Xue,¹ Xisheng Fu,¹ Zhongping Tang,¹ Gen Luo,² Wenjie An,¹ Tao Li,¹ Yi Luo,¹ Xuguang Zhou,¹ and Yi Luo^{2,*}

ABSTRACT

The substituent effect on the structure and property of zinc dialkyldithiophosphates (ZDDPs) have been investigated by DFT calculations. More than ten kinds of substituents including alkyl and aryl groups were chosen for assembling more than twenty ZDDPs. The structural features, thermal decomposition of ZDDP and the hydrolysis of alkaline tetranuclear zinc molecules with various alkyl and aryl substituents have been examined. It is found that the substituents have almost no effect on their central structures, but have significant effect on the thermal decomposition of alkyl- and aryl-substituted ZDDPs and their dimers. The calculations on the hydrolysis of tetranuclear ZDDPs suggest that the reaction free energies are affected by the substituents and the hydrolysis temperature. The radical species derived from ZDDP decomposition tends to be adsorbed on metal surface via multi-coordination manner.

Introduction

Zinc dialkyldithiophosphates (ZDDPs) has been used as an additive for a long time in the formulation of lubricating oils by petrochemical industries.^{1,2} They were originally added to engine oils as antioxidants, as the same role of other antioxidants, such as cuprous dialkyldithiophosphate (CuDDP), organic molybdenum compounds (OMCs), and aromatic amines, *etc.*³⁻⁶ However, it was also found that it can act as a dispersant, a corrosion inhibitor and a detergent, especially as an anti-wear agent.⁷⁻⁹ Due to the two most attractive performances (anti-wear and anti-oxidant functions) of ZDDP additives, they have been attracted much attention and have been widely investigated in the past decades. A good understanding of the substituent effect on the

structure and property of ZDDP would be useful in the intelligent selection and design of alternative anti-wear additives. Although experimental studies are straightforward, they are often time-consuming, expensive, and wearisome. Alternatively, computational chemistry is a useful and powerful approach to obtain valuable information and predict some molecular parameters directly related to the corrosion inhibition behavior of the compounds. The structural features are the fundamental elements to understand the property of compounds. Previously, studies on structural characteristics of ZDDPs performed at several different levels of theory¹⁰⁻¹² showed in good agreement with experimental data. An amount of experimental effort on the study of ZDDP anti-wear additives using various surface analytical techniques has shown that the ZDDP decomposition products rather than ZDDP themselves provide the wear protection.¹³⁻¹⁵ To

have more information about the behavior of ZDDP anti-wear additives, some studies have been performed at finite temperature through ab initio molecular dynamics simulations and static quantum chemical calculations.^{10,11,16-19} These studies gave deep understanding of experimental observations and provided some key insights into the basic chemical behavior of these additives. However, most of these theoretical studies focused on model ZDDP molecules with small alkyl substituents (*i.e.* R = H, Me, *i*Pr *etc.*). Very little is known regarding the effect of larger substituents on the structure and property of ZDDPs, such as C₈, C₁₀, C₁₂ alkyl groups, although such information is crucial for the development of ZDDP additives. In the present study, eleven kinds of substituents including alkyl and aryl groups were chosen for assembling more than twenty zinc compounds. Most of these substituents are often used in the experiment. DFT calculations have been performed on the structural features of these assembled ZDDP monomers. The thermal decomposition of these ZDDP monomers and their dimers and the hydrolysis of tetranuclear zinc alkaline molecules with a variety of alkyl and aryl substituents have been investigated. The information obtained from these calculations could add better understanding to the substituent effect on the structure and property of zinc dialkyldithiophosphates and might provide valuable information on the development of lubricating oil additives.

Computational Details

All calculations were performed with Gaussian 09 software package.²⁰ All of the stationary points were optimized without any geometrical symmetry restriction. Geometrical optimizations were performed using B3LYP functional.^{21,22} Vibrational frequencies were also calculated at the same level of theory in order to confirm each optimized structure as a minimum ($N_{\text{imag}} = 0$) and obtain the thermal correction to the free energy. As for ZDDP monomers and dimers, the 6-31G(d) basis set was used for all nonmetallic atoms and the

relativistic effective core potentials LanL2DZ^{23,24} was considered for Zn atoms. This basis set was called BSI. The bond dissociation energy (BDE), where contains the basis set superposition error (BSSE) correction, was calculated at the same level as that for geometrical optimization. The electronic energies were used for analysis of BDE in this study. In the calculations of tetranuclear dialkyldithiophosphate zinc complex, due to the large molecular size of the complexes (*i.e.* the largest molecule **19** has 479 atoms), the geometrical optimizations and vibrational frequencies were performed at the B3LYP/BSII level. In BSII, the 6-31G(d) basis set was used for O, P, and S atoms and 3-21G(d) was used for C and H atoms of the outermost alkyl group, and LanL2DZ was used for Zn atom. For consideration of aqueous solvation effects during the hydrolysis reaction, the CPCM model^{25,26} was utilized to perform single-point calculations at the level of M06^{27,28}/BSI. The reaction free energies in aqueous solution were obtained from such single-point calculations, and the gas-phase Gibbs free energy corrections were included. In the calculations of metal surface adsorption part, Fe₅ cluster, which has the structural features of Fe(100) surface, was used as a metal surface model to investigate the interaction energy of ZDDP with metal surface as well as the adsorption behavior of the radical species. Because of the complexity and time consuming of the calculation, a cluster of iron consisting of five atoms (1,4) with spin multiplicity of five was chosen for the calculation, as adopted in the previous work.²⁹ In this part, the LanL1MB pseudopotential basis set³⁰ was used for Fe atoms and the 6-31G(d) (for C, H, O, and P)/LanL2DZ (for Zn) basis sets were used for the atoms of ZDDP molecule. To consider the adsorption of active elements (O and S) at metal cluster, the scan energy curves for Fe...O and Fe...S distances between ZDDP and Fe₅ cluster were carried out and the minimum energy point was chosen as the minima structure for obtaining the adsorption energy.

Results and Discussion

Structure and thermal decomposition investigation of ZDDP monomers

The structural aspects of the monomers are of significant interest in the study of ZDDPs and have been the focus of several previous theoretical and experimental investigations.^{10-12,31,32} The structure of ZDDP monomer has been well established and its general structure is shown in Figure 1. The two dialkyldithiophosphate (DDP) ligands chelate Zn atom by the two S atoms in each DDP ligand and the orientation of the two DDP ligands is perpendicular.

Figure 1. General structure of ZDDP monomer.

Chart 1. Substituents used in this study.

To have a better understanding of the effect of R groups on the structural aspects, eleven alkyl and aryl groups (see Chart 1), which often appears in the experimentally used ZDDP, were chosen for investigating the structures. Eleven ZDDP monomers (compounds **1–11**) comprised by one or two kinds of R groups were optimized by DFT calculations. In the case of large alkyl substitutes, only the most stable conformer with zigzag alkyl chain was considered. The important bond lengths of such monomers are collected in Table 1. The data in this table shows that the P–S bond lengths are 2.02–2.04 Å and the Zn–S bond lengths are 2.46–2.48 Å for all complexes. The difference in the bond lengths of ZDDP monomers with various substituents is less than 0.03 Å, suggesting that the R groups

have very little effect on the geometric parameters of ZDDP core structures.

It is generally accepted that ZDDPs undergo decomposition under engine operation conditions, such as high temperature and high pressure. The further reaction of these decomposition products could lead to the formation of zinc poly(thio)phosphate film.³³⁻³⁸

A molecular-level examination of thermostability of ZDDP monomers with various of substituents may provide useful information on the behavior of their thermal decomposition. In this part, we evaluated the possible decomposition pathways by bond dissociation energy of the key bonds of ZDDP molecules. As shown in Scheme 1, several possible dissociation manners were considered by DFT calculations. Paths **a** and **b** are the dissociation of Zn–S bond via homolysis and heterolysis manners, respectively. The homolysis of Zn–S bond results in DDP• and Zn-DDP• radical fragments. The homolysis of P–S bond could form (RO)₂PS• and (DDP)ZnS• (Path **c**). The other two kinds of homolysis of P–O (Paths **d** and **e**) and C–O (Paths **f** and **g**) bonds lead to the loss of alkoxy/aryloxy and alkyl/aryl radicals, respectively. All these possible dissociation pathways were calculated and the results were listed in Table 2.

As shown in Table 2, for all substituted ZDDP monomers, the bond dissociation energies (BDEs) of heterolysis of Zn–S bonds are as high as 165–174 kcal/mol, which are significantly higher than that for their corresponding homolysis manners (*ca* 75–76 kcal/mol). Therefore, the homolysis manner of ZDDP monomers is more likely to occur. The BDEs of homolysis of P–S bonds are 82–85 kcal/mol for all cases (Path **c** in Table 2). The homolysis of P–O and C–O bonds via Paths **d** to **f** have similar BDE values (79–87 kcal/mol,) when both R_a and R_b are alkyl groups (compounds **1–8** in Table 2). The result suggests that the homolysis of P–O and C–O bonds are competitive and the homolysis of Zn–S bonds, forming DPP• radical, is the main decomposition manner when both R_a and R_b are alkyl groups. However, the aryl

Table 1. Selected Bond Lengths of the ZDDP Monomers.^[a]

Compounds	Substituents	Bond length (Å)							
		P1-S1	P1-S2	P2-S3	P2-S4	Zn-S1	Zn-S2	Zn-S3	Zn-S4
1	R _a = R1, R _b = R2	2.029	2.031	2.041	2.028	2.474	2.471	2.469	2.462
2	R _a = R2, R _b = R4	2.027	2.028	2.040	2.025	2.472	2.476	2.469	2.465
3	R _a = R2, R _b = R3	2.027	2.027	2.039	2.026	2.471	2.476	2.469	2.463
4	R _a = R1, R _b = R4	2.029	2.029	2.041	2.027	2.471	2.474	2.469	2.463
5	R _a = R _b = R5	2.027	2.027	2.040	2.026	2.472	2.475	2.469	2.464
6	R _a = R _b = R6	2.027	2.027	2.040	2.027	2.473	2.475	2.470	2.462
7	R _a = R1, R _b = R9	2.029	2.030	2.042	2.027	2.473	2.474	2.467	2.463
8	R _a = R1, R _b = R10	2.032	2.033	2.040	2.028	2.468	2.475	2.470	2.463
9	R _a = R _b = R7	2.019	2.020	2.028	2.021	2.479	2.474	2.470	2.466
10	R _a = R1, R _b = R7	2.027	2.025	2.035	2.026	2.479	2.470	2.469	2.462
11	R _a = R1, R _b = R8	2.027	2.025	2.036	2.027	2.478	2.470	2.469	2.462

[a] Atom labeling defined in Figure 1.

Scheme 1. Possible Dissociation Manners for the ZDDP Monomers.

substituents would significantly reduce the BDEs of the homolysis of P–O bonds and increase the BDEs of C–O bonds. The BDE calculations of compounds **9–11** show that the BDEs of the homolysis of P–O bonds (Path **e**) are 64–66 kcal/mol, which are even lower than that of Zn–S bond homolysis. The BDEs of the homolysis of C–O bonds (Path **g**) are *ca* 92 kcal/mol. Therefore, the loss of aryloxy radicals is favored over the loss of aryl radicals for aryl

substituted ZDDP monomers investigated in this study. The homolysis of P–O bonds, forming RO[•] radical, is the main decomposition manner when aryl substituents are present in the ZDDP molecules, which is different from that of the homolysis of Zn–S bonds for the full-alkyl substituted ZDDPs. It is noted that, in the resulting DDP anion or radical, the charge or unpaired electron delocalized on both S atoms (see Figure S1 in SI).

Table 2. Bond Dissociation Energy (BDE, kcal/mol) of the Main Chemical Bonds of the ZDDP Monomers in Different Dissociation Manners.^[a]

Compounds	Substituents	BDE in different dissociation manners						
		a	b	c	d	e	f	g
1	R _a = R1, R _b = R2	169.9	76.1	84.7	82.3	83.1	84.5	86.5
2	R _a = R2, R _b = R4	169.8	75.9	84.3	83.7	83.6	86.6	86.2
3	R _a = R2, R _b = R3	169.8	76.0	84.6	83.6	83.7	86.5	86.2
4	R _a = R1, R _b = R4	169.6	75.9	84.3	83.5	83.3	84.6	86.3
5	R _a = R _b = R5	169.2	75.9	84.6	83.6	83.6	86.4	86.4
6	R _a = R _b = R6	169.2	75.9	84.6	83.6	83.6	86.5	86.5
7	R _a = R1, R _b = R9	167.0	76.1	84.2	82.6	82.9	84.9	78.9
8	R _a = R1, R _b = R10	167.4	76.0	84.0	81.4	80.8	84.7	80.8
9	R _a = R _b = R7	165.2	75.0	82.5	65.8	65.8	92.6	92.6
10	R _a = R1, R _b = R7	173.8	75.8	84.5	82.1	65.2	84.6	92.9
11	R _a = R1, R _b = R8	167.1	75.7	84.4	82.0	64.2	84.4	93.0

[a] Dissociation manners defined in scheme 1.

Scheme 2. Possible Dissociation Processes for the ZDDP Dimers.

To evaluate the effect of basis set, a larger basis set 6-311+G(d,p) for nonmetallic atoms and LanL2DZ for Zn atom were used for calculation of several smaller ZDDP monomers. The results show that the usage of larger basis set doesn't alter the results derived from smaller basis set (see Tables S1 and S2 in supporting information). Therefore, the reported results at the level of B3LYP/BSI could be reliable.

Thermal decomposition investigation of ZDDP dimers

It is well known that ZDDP molecules exist in solution not only as monomers but also as

dimers or even higher order oligomers.³⁹⁻⁴¹ Based on information obtained through experimental⁴²⁻⁴⁴ and theoretical investigations,^{32,45} it is known that the ZDDP dimer $\text{Zn}_2[\text{PS}_2(\text{OR})_2]_4$ possesses two bridging DDP ligands connecting the two Zn atoms and two terminal DDP ligands chelating each Zn atom (Scheme 2). Although the structures of ZDDP dimers are well established, there is very limited information on their thermal decomposition behavior. In the above section, we have carefully examined the thermal decomposition behavior of ZDDP monomers, and it is found that the homolysis of Zn-S and P-O bonds are the main decomposition manner

of ZDDPs with different kinds of substituents. Based on this result, only the homolysis of Zn–S and P–O bonds, including the bridging and terminal DDP ligands, were considered in ZDDP dimer cases. As shown in Scheme 2, the Paths **a** and **b** are the homolysis of Zn–S bonds of bridging and terminal DDP ligands, respectively. The Paths **c** and **d** are the homolysis of P–O bonds of terminal DDP ligands and the Paths **e** and **f** are the homolysis of P–O bonds of bridging DDP ligands.

The data showed in Table 3 indicates that the BDE values for the dissociation of terminal DDP ligands (*ca* 75 kcal/mol, Path **a**) are very similar to that for ZDDP monomers (Path **b** in Table 2). By contrast, the BDE values for the dissociation of bridging DDP ligands are *ca* 96 kcal/mol, which is *ca* 20 kcal/mol higher than that for the terminal cases. This means that the bridging DDP ligands are more stable than terminal ones. For all the homolysis of P–O bonds in ZDDP dimers, the BDEs are 82–85 kcal/mol, which are similar to that in ZDDP monomers. The values suggest that the dissociation of terminal DDP ligands is the main decomposition manner when both R_a and R_b are alkyl groups (compound **12** in Table 3). As expected, the aryl substituents significantly reduce the stability of P–O bonds, as suggested by the BDE values (65–67 kcal/mol, compounds **13–15** in Table 3). The loss of aryloxy radicals (*ca* 65–67 kcal/mol) is favored over the loss of aryl radicals (83–85 kcal/mol) for aryl substituted ZDDP dimers. Similar to ZDDP monomers, the of P–O bond homolysis leading to $RO^\bullet$ radical is the main decomposition manner when aryl substituents are present in the ZDDP molecules.

The hydrolysis reaction of tetranuclear dialkyldithiophosphate zinc complexes

It is known that tetranuclear alkaline ZDDPs with $[Zn_4(\mu_4-O)]$ core structure could be formed by a spontaneous precipitation from the corresponding initial liquid binuclear complexes as a result of oxidation by atmospheric oxygen.⁴⁶ The structures of tetranuclear Zn(II) dialkyldithiophosphate complexes, $[Zn_4X\{S_2P(OR)_2\}_6]$ ($X = O, S$), have been studied.

And, the result showed that these tetranuclear complexes possess six bridging ligands and a central sulfur or oxygen atom coordinates to four Zn atoms.^{47–49} O'Brien and co-workers reported that the X-ray single crystal structures of a series of tetranuclear Zn complexes, viz., $[Zn_4(\mu_4-O)(O_2CNEt_2)_6]$, $[Zn_4(\mu_4-O)(S_2PEt_2)_6]$, and $[Zn_4(\mu_4-O)(S_2CNEt_2)_6]$.⁵⁰ Rheingold *et al* isolated the complex $Zn_4(\mu_4-O)[O_2P(O^tBu)_2]_6$ ⁵¹ and provided the structural information of solid tetranuclear Zn complexes. Experimentally, the hydrolysis reaction of tetranuclear dialkyldithiophosphate Zn complexes could occur to yield two molecules of dinuclear Zn complexes: $Zn_4(\mu_4-O)[S_2P(OR_a)(OR_b)]_6 + H_2O \rightarrow 2 Zn_2(\mu_2-OH)[S_2P(OR_a)(OR_b)]_3 + \Delta G$ (reaction free energy). However, there is little available information about the effect of R (alkyl and aryl) groups of the DDP ligands. In this study, the hydrolysis reaction of six tetranuclear dialkyldithiophosphate Zn complexes with different R groups was computed under the temperature range of 40–120 °C. The computed reaction free energies are illustrated in Table 4 and Figure 2.

As shown in Table 4, when the R groups are isopropyl (C3) and *n*-butyl (C4), the hydrolysis reaction (ΔG_1) of compound **16** is endothermic by 12.3 kcal/mol at the 40 °C. When the R groups are large alkyl groups, *i.e.* isopentyl (C6), isodecyl (C8), and *n*-dodecyl (C12), the hydrolysis free energies (ΔG_2 to ΔG_4) of compounds **17–19** are lower than that of compound **16** with small substituent groups (ΔG_1) at the same temperature. It is noteworthy that the aryl groups could increase the hydrolysis stability of tetranuclear alkaline ZDDPs. The reaction free energies (ΔG_5 and ΔG_6) of aryl substituted alkaline ZDDPs **20** and **21** are obviously higher than that of full-alkyl substituted complexes (**16–19**). Figure 2 clearly illustrates that the reaction free energies of all tetranuclear alkaline ZDDPs decrease with the increase of hydrolysis temperature. Obviously, the hydrolysis reaction of **18** becomes an exothermic reaction when the temperature increases to 120 °C. As for compound **19**, the

Table 3. Bond Dissociation Energy (BED, kcal/mol) of the Main Chemical Bonds of the ZDDP Dimers in Different Dissociation Manners.^[a]

Compounds	Substituents	BDE in different dissociation manners					
		a	b	c	d	e	f
12	R _a = R2, R _b = R1	75.7	96.5	83.7	84.6	83.2	82.9
13	R _a = R7, R _b = R1	75.2	96.6	66.6	83.9	65.5	83.0
14	R _a = R8, R _b = R1	75.1	96.4	65.4	83.9	64.4	82.9
15	R _a = R _b = R7	75.7	96.6	66.3	66.3	65.3	65.3

[a] Dissociation manners defined in scheme 2.

Table 4. The Reaction Free Energy (kcal/mol) for the Hydrolysis of Tetranuclear Zn Complexes under Different Temperature.

Compounds	Substituents	ΔG	Temperature (°C)								
			40	50	60	70	80	90	100	110	120
16	R _a = R1, R _b = R2	ΔG_1	12.3	11.8	11.4	10.9	10.5	10.0	9.6	9.1	8.7
17	R _a = R _b = R4'	ΔG_2	10.6	10.2	9.8	9.4	9.0	8.6	8.2	7.8	7.3
18	R _a = R _b = R5	ΔG_3	5.8	5.0	4.3	3.6	2.8	2.1	1.3	0.6	-0.1
19	R _a = R _b = R6	ΔG_4	2.3	1.7	1.0	0.4	-0.3	-1.0	-1.6	-2.3	-2.9
20	R _a = R1, R _b = R7	ΔG_5	14.7	14.3	14.0	13.7	13.4	13.0	12.7	12.4	12.1
21	R _a = R1, R _b = R8	ΔG_6	17.4	17.1	16.8	16.6	16.3	16.1	15.8	15.6	15.3

hydrolysis reaction is exothermic when the temperature reaches 80 °C. Based on these results, we can conclude that large alkyl groups and high temperature would promote the hydrolysis reaction of tetranuclear dialkyldithiophosphate Zn complexes and aryl groups could restrain the hydrolysis reaction to occur in comparison with full-alkyl substituted cases.

The adsorption behavior of ZDDP monomer on the metal surface

The ZDDP molecules containing hetero-atoms (P, S, O) could adsorb on metallic surfaces under engine conditions or similar conditions in the laboratory. Iron surface is one of the most common metal surfaces and Fe₅ cluster having the features of Fe(100) surface (Figure 3) was considered for investigating the interaction between ZDDP and metal surface.^{29,52} To investigate the adsorption capacity of different hetero-atoms of ZDDP molecules, the model ZDDP molecule [(Me₂O)PS₂]₂Zn was used for the calculation. Since P atoms is surrounded by O and S atoms and therefore is difficult to directly

interact with metal surface before ZDDP decays. Therefore, only the adsorption of active element O and S over Fe₅ cluster were considered. The rigid scan of O...Fe and S...Fe distances between ZDDP and Fe₅ cluster were performed. In such calculations, the Fe₅ cluster was fixed and the specified O or S atom of ZDDP was placed at the above of top-Fe atom of Fe₅ cluster in the initial model.

Figure 2. The reaction free energy (kcal/mol) for the hydrolysis of tetranuclear Zn complexes under different temperatures.

Figure 3. Fe (100) surface and its model structure (Fe_5 cluster).

As shown in Figure 4, the minimum energy point in the scan curve was chosen as the minima structure for obtaining the adsorption energy. The adsorption energy (E_{int}) of O (or S) atom was estimated by the energy difference between the energy of the lowest point in the scan curve and the energy sum of isolated ZDDP and Fe_5 cluster.

As illustrated in Figure 4a, the O atom of ZDDP gradually gets close to the Fe atom of Fe_5 cluster from 2.65 Å to 2.05 Å (step size = 0.02 Å). The corresponding energy curve shows that the energy reduces as the O...Fe distance reduces from 2.65 Å to 2.45 Å and the energy increases as the O...Fe distance further reduces. Therefore, the minimum energy point (O...Fe distance of 2.45 Å) in scan curve could be used to estimate the adsorption energy of O atom. The adsorption energy of O atom is calculated to be 19.3 kcal/mol.

As for the scan of the S...Fe distance, the S atom of ZDDP gradually gets close to the Fe atom of Fe_5 cluster from 2.80 Å to 2.20 Å (step size = 0.02 Å). Similar to the scan of O...Fe distance, the energy reduces as the S...Fe distance reduces from 2.80 Å to 2.44 Å and the energy increases as the S...Fe distance further reduces (Figure 4b). It is obvious that the energy curve for S atom adsorption is steeper in comparison with that of O atom adsorption. The adsorption energy of S atom was calculated to be 97.1 kcal/mol, which is significantly larger

Figure 4. The scan energy curve for Fe...O (a) and Fe...S distance (b) between ZDDP and Fe_5 cluster.

than that of O atom case (19.3 kcal/mol). This result indicates that both O and S atoms of ZDDP molecule can adsorb on the metallic surfaces and the S atom adsorption could more easily occur than the O atom adsorption, as suggested by their adsorption energies (97.1 vs 19.3 kcal/mol).

Figure 5. Structures and their complexation energies (kcal/mol) of the complexes of Fe_5 cluster with radical fragments derived from ZDDP decomposition.

It is generally considered that ZDDPs decompose under normal engine conditions and the decomposition products form “pads” on engine parts to protect the underlying material.⁵³⁻⁵⁶ As mentioned above, the ZDDP

monomers possibly form $\text{RO}^\bullet$, $(\text{RO})_2\text{PS}_2^\bullet$, and $(\text{RO})_2\text{PS}^\bullet$ radicals by the homolysis of P–O, Zn–S, and P–S bonds, respectively. To get better understanding of the complexation between organic radical fragments and iron surface, the

isopropyl-substituted species were studied for the complexation with Fe₅ cluster. In species ⁱPrO[•] (species A), the O atom could simultaneously interact with three Fe atom of Fe₅ cluster to form **Int1** (Figure 5) and the complexation process is significantly exergonic by 89.3 kcal/mol. As for the species (ⁱPrO)₂PS₂[•] (species B) and (RO)₂PS[•] (species C), they can form several complexes due to more than one active atoms and multiple complexation manners. As illustrated in Figure 5, the species B and Fe₅ cluster could form complexes **Int2–Int5** and the complexes **Int6–Int10** could be formed between species C and Fe₅ cluster. All these complexation processes are exothermic and the complexes adopt multi-coordinating manners. In the case of species B, the most stable complex is **Int5**, in which the three active atoms (S, S, and O) interact with three Fe atoms of Fe₅ cluster. In the case of species C, **Int6**, **Int9**, and **Int10** show a great stability and the formation of these three complexes are exothermic by about 120 kcal/mol. It is noted that, due to the computational limitation, only Fe₅ cluster was chosen as a model of iron surface, which was also applied in previous studies.^{29,52} The multi-coordination behavior mentioned here can be regarded as that the studied radical fragments prefer to adsorb on multi-site Fe atoms at the first-layer of iron surface, where the sub-surface was not considered. The results shown in Figure 5 could help us to understand the subsequent adsorption behavior of the resulting organic radical fragments on iron surface.

Conclusions

In this work, the structural features of various ZDDP monomers, the thermal decomposition of ZDDP monomers and their dimers, and the hydrolysis of alkaline tetranuclear zinc molecules with various alkyl and aryl substituents have been investigated by DFT calculations. The following conclusions could be drawn:

- (1) The computational results suggest that both alkyl and aryl substituents have very little effect on geometric parameters of their core

structures. The important bond lengths of P–S and Zn–S bonds are 2.02–2.04 Å and 2.46–2.48 Å, respectively. However, the alkyl and aryl substituents have significant effect on the thermal decomposition of ZDDP monomers. It has been found that, for full-alkyl substituted ZDDP molecules, the main decomposition manner is the homolysis of Zn–S bond, leading to DPP radicals. Whereas, the P–O bond homolysis giving alkoxy radicals is favored for aryl substituted ZDDPs considered in this study.

- (2) In ZDDP dimers, the homolysis of Zn–S bond of the terminal DDP ligands is much easier than that of bridging DDP ligands. The data shows that most decomposition manners of ZDDP dimers are the loss of DDP radicals and aryloxy radicals for alkyl- and aryl-substituted ZDDP molecules, respectively.
- (3) The hydrolysis reaction of tetranuclear dialkyldithiophosphate Zn complexes becomes easier when the length of alkyl chain increases. Full-alkyl substituted molecules are easier to hydrolyze than aryl-contained ones. In all cases, the hydrolysis reaction free energy reduces when the hydrolysis temperature increases.
- (4) The active element O and S could easily interact with metal cluster. The calculated adsorption energy indicates that S atom is easier to interact with Fe₅ cluster than O atom. In addition, the current calculations also suggest that the organic radical fragments derived from ZDDP also tend to be adsorbed on metal surface via multi-coordination manner.

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Keywords: Zinc dialkyldithiophosphates (ZDDPs), Substituent effect, Thermal decomposition, Hydrolysis reaction, DFT

References and Notes

1. C. N. Rowe, J. J. Dickert, *ASLE Trans.* **1967**, *10*, 85.
2. J. Sato, M. Shima, T. Sugawara, A. Tahara, *Wear* **1982**, *52*, 52.
3. K. U. Ingold, *Chem. Rev.* **1961**, *61*, 563.
4. Y. Luo, S. Maeda, K. Ohno, *J. Phys. Chem. A* **2008**, *112*, 5720.
5. A. Kassler, E. Pittenauer, N. Doerr, G. Allmaier, *Rapid Commun. Mass Sp* **2014**, *28*, 63.
6. Z. Tang, Q. Kong, Y. Luo, W. Xue, J. Qu, H. Chen, X. Fu, *J. Theor. Comput. Chem.* **2014**, *13*, 14500035.
7. W. J. Bartz, *Engine Oils and Automotive Lubrication*; Marcel Dekker: New York, **1993**.
8. D. Klamman, Ed. *Lubricants and Related Products*; Weinheim: Deerfield Beach, FL, **1984**.
9. H. C. Freuler, U.S. Patent 2364283, **1944**.
10. N. J. Mosey, T. K. Woo, *J. Phys. Chem. A* **2004**, *108*, 6001.
11. N. J. Mosey, T. K. Woo, *J. Phys. Chem. A* **2003**, *107*, 5058.
12. D. R. Armstrong, E. S. Ferrari, K. J. Roberts, D. Adams, *Wear* **1997**, *208*, 138.
13. R. J. Bird, G. P. Galvin, *Wear* **1976**, *37*, 143.
14. P. A. Willermet, J. M. Pierprzak, D. P. Dailey, R. O. Carter, N. E. Lindsay, L. P. Haack, J. E. De Vries, *ASME Trans.* **1991**, *113*, 38.
15. P. A. Willermet, R. O. Carter, E. N. Boulos, *Tribol. Int.* **1992**, *25*, 371.
16. N. J. Mosey, T. K. Woo, *Tribol. Int.* **2006**, *39*, 979.
17. N. J. Mosey, M. H. Müser, T. K. Woo, *Science* **2005**, *307*, 1612.
18. F. M. Bickelhaupt, E. J. Baerends, *Rev. Comput. Chem.* **2000**, *15*, 1.
19. R. Car, M. Parrinello, *Phys. Rev. Lett.* **1985**, *55*, 2471.
20. M. J. Frisch, et al. *Gaussian 09, Revision D.01*, Gaussian, Inc., Wallingford CT, 2009.
21. C. Lee, W. Yang, R. G. Parr, *Phys. Rev.* **1988**, *B37*, 785.
22. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648.
23. W. R. Wadt, P. J. Hay, *J. Chem. Phys.* **1985**, *82*, 284.
24. P. J. Hays, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.
25. V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995.
26. M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669.
27. Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157.
28. Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.
29. M. Mousavi, H. Safarizadeh, A. Khosravan, *Corrosion Science* **2012**, *65*, 249.
30. P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.
31. N. E. Gallopoulos, *Am. Chem. Soc., Div. Petrol. Chem., Prepr.* **1966**, *11*, 21.
32. S. Jiang, S. Dasgupta, M. Blanco, R. Frazier, E. S. Yamaguchi, Y. Tang, W. A. Goddard III, *J. Phys. Chem.* **1996**, *100*, 15760.
33. M. Fuller, L. R. Fernandez, G. R. Massoumi, W. N. Lennard, M. Kasrai, G. M. Bancroft, *Tribol. Lett.* **2000**, *8*, 187.
34. M. L. Suominen Fuller, M. Kasrai, G. M. Bancroft, K. Fyfe, K. H. Tan, *Tribol. Int.* **1998**, *31*, 627.
35. Z. F. Yin, M. Kasrai, M. Fuller, G. M. Bancroft, K. Fyfe, K. H. Tan, *Wear* **1997**, *202*, 172.
36. P. A. Willermet, R. O. Carter III, P. J. Schmitz, W. Zhu, *Tribol. Int.* **1995**, *28*, 177.
37. W. A. Glaeser, D. Baer, M. Engelhardt, *Wear* **1993**, *162-164*, 132.
38. P. A. Willermet, R. O. Carter III, E. N. Boulos, *Tribol. Int.* **1992**, *25*, 371.
39. P. G. Harrison, P. Brown, J. McManus, *Inorg. Chim. Acta* **1992**, *202*, 3.

40. P. G. Harrison, P. Brown, M. J. Hynes, J. M. Kiely, J. McManus, *J. Chem. Res., Synop.* **1991**, 174.
41. P. G. Harrison, A. Sebal, *J. Chem. Res., Synop.* **1991**, 340.
42. S. L. Lawton, G. T. Kokotailo, *Inorg. Chem.* **1969**, 8, 2410.
43. T. Ito, T. Igarashi, H. Hitosi, *Acta Crystallogr., Sect. B* **1969**, B25, 2303.
44. A. V. Ivanov, O. N. Antzutkin, A.-C. Larsson, M. Kritikos, W. Forsling, *Inorg. Chim. Acta* **2001**, 315, 26.
45. D. R. Armstrong, E. S. Ferrari, K. J. Roberts, D. Adams, *Wear* **1997**, 208, 138.
46. A. V. Ivanov, O. N. Antzutkin, A. Larsson, M. Kritikos, W. Forsling, *Inorg. Chim. Acta* **2001**, 315, 26.
47. Ph. G. Harrison, M. J. Begley, T. Kikabhai, F. Killer, *J. Chem. Soc., Dalton Trans.* **1986**, 925.
48. J. Burn, G. W. Smith, *Chem. Commun. (London)* **1965**, 394.
49. A.-C. Larsson, A. V. Ivanov, W. Forsling, O. N. Antzutkin, A. E. Abraham, A. C. de Dios, *J. Am. Chem. Soc.* **2005**, 127, 2218.
50. M. A. Malik, P. O'Brien, M. Motevalli, I. Abrahams, *Polyhedron* **2006**, 25, 241.
51. C. G. Lugmair, T. D. Tilley, A. L. Rheingold, *Chem. Mater.* **1997**, 9, 339.
52. M. R. Arshadi, M. Lashgari, Gh. A. Parsafar, *Mater. Chem. Phys.* **2004**, 86, 311.
53. K. Varlot, M. Kasrai, J. M. Martin, B. Vacher, G. M. Bancroft, E. S. Yamaguchi, P. R. Ryason, *Tribol. Lett.* **2000**, 8, 9.
54. A. G. Papay, *Lubr. Sci.* **1998**, 10, 209.
55. P. A. Willermet, J. M. Pieprzak, D. P. Dailey, R. O. Carter III, N. E. Lindsay, L. P. Haack, J. E. DeVries, *ASLE Trans.* **1991**, 113, 38.
56. R. J. Bird, G. P. Galvin, *Wear* **1976**, 37, 143.

GRAPHICAL ABSTRACT

Computational Studies on the Effects of Substituents on the Structure and Property of Zinc Dialkyldithiophosphates

Weiguo Xue, Xisheng Fu, Zhongping Tang, Gen Luo, Wenjie An, Tao Li, Yi Luo, Xuguang Zhou, and Yi Luo,*

The substituent effect on the structure and property of zinc dialkyldithiophosphates (ZDDPs) was investigated by DFT calculations. The results indicate that the substituents have very little effect on their structures, but have significant effect on the thermal decomposition of alkyl- and aryl-substituted ZDDPs and their dimers. The hydrolysis reaction free energies of tetranuclear dialkyldithiophosphate zinc complexes are affected by the substituents and the hydrolysis temperature.

DFT Study

The substituent effect on
the structure and property of
ZDDPs