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Formation of Zinc Phosphate Polymers and Networks through the Insertion of Metathiophosphates into Zinc Dialkyldithiophosphates

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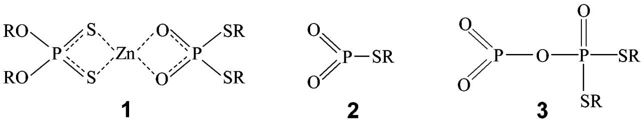
The interactions between metathiophosphates (MTPs) and zinc dialkyldithiophosphates (ZnDDPs) were explored through molecular simulation. The results highlight a novel reaction leading to the formation of zinc phosphate polymers and networks through the insertion of MTPs into ZnDDPs.

Metal phosphates (MPs) comprise an important class of inorganic substances used in many applications of technological relevance. Crystalline MPs are used in heterogeneous catalysis,[1] molecular sorption,[2] and various emerging technologies.[3] Amorphous MPs, on the other hand, are employed in automobile engines as antiwear films,[4] in several optical applications,[5] and in biological implants.[6] Although several protocols for the synthesis of MPs have been developed,[7] the underlying chemical processes involved in these procedures remain poorly understood. This is due primarily to the large number of variables associated with these reactions, coupled with the difficulty in examining these systems under typical reaction conditions.[8] It is clear that further insight is required to understand MP formation, optimize synthetic strategies, and design new MPs rationally. In this context, the identification of reactions that lead to the formation of complex MP structures from simple molecular components will prove invaluable. In what follows, we report the results of ab initio molecular dynamics (AIMD) simulations and static quantum chemical calculations that suggest a novel reaction pathway leading to zinc phosphate polymers and networks.

Chart 1



1 **2** **3**

Previously, we have performed several theoretical investigations into the role of zinc dialkyldithiophosphates (ZnDDPs) as antiwear additives in motor oils, which form protective zinc phosphate films on engine surfaces.[9−11] In one of our previous studies,[11] it was found that **1**, a slightly more thermodynamically stable isomer of ZnDDP, can decompose spontaneously at elevated temperatures through the elimination of metathiophosphates (MTPs, **2**), which, in turn, can react with other molecules of **2** to yield phosphate chains (**3**).[12] Such a reaction may prove useful in the formation of MPs; however, it requires the accumulation of large quantities of **2** in solution, which is unlikely considering the high reactivity of this species. In the simulations presented here, the direct reaction of **1** with **2** is examined as a possible means of producing **3**, plus (*O*,*O*-DDP)-Zn-SR,[13] without forming **2** in high concentrations. Basically, it is anticipated that the interaction of **2** with **1** will prompt the elimination of a second molecule of **2** from **1**, and polymerization of the MTPs will follow to yield **3**. Interestingly, the expected scenario does not occur, but rather an unforeseen reaction is observed that yields MP chains through the insertion of **2** into **1**. Although the simulations were performed in the context of antiwear films, this formation mechanism that was observed is of much broader interest, as noted above.

Car−Parrinello AIMD simulations[14] were performed on a system composed of one molecule each of **1** and **2** using

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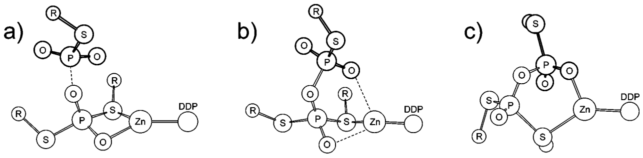

Figure 1. Key structures observed during the AIMD simulation: (a) the adduct formed between **1** and **2**; (b) the insertion of **2** into **1**; (c) the final product. R = methyl; DDP = $S_2P(OR)_2^-$. In all structures, the atoms originally in **2** are designated with thicker lines.

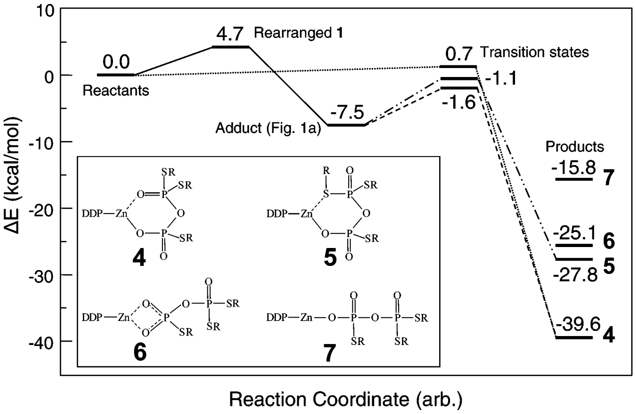

Figure 2. Relative electronic energies of the stationary points along the reaction pathways located for the insertion of **2** into **1**. The direct insertion pathway is indicated with the dotted line, the process involving Zn−O bond dissociation following rearrangement is denoted by the dash-dotted line, and that involving Zn−S bond dissociation is given by the dashed line. Steps common to both processes that involve rearrangement are connected with solid lines. Energies relative to the separate reactants are provided at each stationary point in kcal/mol. R = methyl; DDP = $S_2P(OR)_2^-$.

the CPMD software package.[15] The potential energy and nuclear forces were calculated with the PBE gradient-corrected density functional[16] in conjunction with analytical pseudopotentials[17] and a plane-wave basis set. The simulations were performed under NVE conditions with the initial temperature of the system set to 500 K. The distance between the phosphorus atom of **2** and that in the *S*,*S*-DDP ligand of **1** was constrained such that it was only allowed to decrease throughout the simulation. The selection of this distance was based simply upon the notion that to form **3**, the P atoms in **1** and **2** must approach one another. The application of the constraint in a slow-growth fashion promotes the occurrence of chemical reactions on the time scales accessible in the simulations (tens of picoseconds) and allows for unforeseen chemical events to occur. Full details of the calculations are provided as the Supporting Information.

Key structures observed during the AIMD simulations are given in Figure 1. A movie of the simulated trajectory is provided as the Supporting Information. At an early stage, **1** underwent an intramolecular rearrangement such that the *S*,*S*-DDP ligand was coordinated to zinc through an oxygen and a sulfur (structure not shown). This process has been discussed elsewhere.[11] The two reactants then formed an adduct (Figure 1a) in which the phosphorus atom of **2** was coordinated by one of the oxygen atoms in the *S*,*S*-DDP group of **1**. Once this intermediate was formed, dissociation of the remaining Zn−O bond in **1** occurred along with the attack of the zinc by one of the oxygen atoms originally in **2** (Figure 1b). The product of this reaction is shown in Figure 1c. Continuing the simulation showed that the newly formed Zn−O bond persisted in the absence of the geometric constraint, while the Zn−S bond dissociated, allowing for additional changes in the coordination at Zn to occur.

The reaction observed during the AIMD simulations is consistent with the insertion of **2** into one of the Zn−O bonds between the Zn atom and the *S*,*S*-DDP ligand in **1**. To the best of our knowledge, this reaction has not been reported previously in phosphate chemistry. However, the observed chemical process is reminiscent of reactions that are employed extensively in transition-metal-catalyzed polymerization.[18,19] By analogy, we suggest that the observed reaction may be useful in the formation of MP chains and networks from simple phosphate precursors.

The AIMD simulations indicated that the product of the insertion reaction may adopt a number of different conformations. Relevant structures are labeled **4**−**7** in Figure 2. It is also clear that the formation of these products may occur through any of several distinct mechanistic pathways. The transition from the intermediate structure (Figure 1a) to a product can occur through either the dissociation of a Zn−O bond, which was observed during the AIMD simulations and yields **5**, or the dissociation of a Zn−S bond, which would yield **4**. Furthermore, the direct insertion of **2** into one of the Zn−O bonds in **1** to yield **4** could also occur without rearrangement or the formation of an intermediate. Once either of products **4** or **5** is formed, transformation to **6** or **7** can take place readily. To gain further insight into these possibilities, the relative energies of the products and stationary points along the prospective mechanistic pathways were evaluated at the B3LYP/LACV3P+(d,p) level of theory[20,21] using the Jaguar software package.[22] Full details of the calculations are provided as the Supporting Information. The results of these calculations are summarized in Figure 2.

The reaction energies favor the formation of **4**, which can be understood in terms of the geometric and electronic structures of species **4**−**7**. Essentially, in **4** there exists one well-formed Zn−O bond, a dative Zn−O bond with favorable atomic charges, and a six-membered ring. By comparison, in **5** electrostatic repulsion between the Zn and S atoms in the Zn−S bond will exist because the sulfur formally has a positive charge, in **6** there will be significant strain within the four-membered ring and a fully formed Zn−O bond is not present, and in **7** the number of bonding interactions at

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Zn is decreased altogether. Each of these factors destabilizes products **5**−**7** relative to **4**.

On the electronic potential energy surface, the transition state for the direct insertion of **2** into a Zn−O bond is of lower energy than the rearranged form of **1** and, hence, the direct insertion mechanism is favored. However, if the rearranged form of **1** is attained, a stable adduct can be formed (similar to Figure 1a). Progression from this adduct to the product is favored to occur through the dissociation of the Zn−S bond ($\Delta E^{\ddagger} = 5.9$ kcal/mol), while the process involving Zn−O dissociation has a slightly larger barrier of 6.4 kcal/mol. Thus, the formation of **4** is favored kinetically regardless of whether insertion occurs through a direct or stepwise process.

When free energies are considered (see Figures S1 and S2 of the Supporting Information for examples at 300 and 500 K), the transition state along the direct insertion pathway is significantly higher in energy than the rearranged form of **1**. Hence, the preferred reaction pathway will be determined by the relative energies of the transition states. At both temperatures considered, the lowest energetic barrier is incurred through the stepwise mechanism involving rearrangement followed by Zn−S bond dissociation to yield **4**, and thus this process is favored. These results are consistent with the AIMD simulations, where a stepwise insertion process was observed. During those simulations, however, the transition from the adduct to the product occurred through Zn−O bond dissociation, as opposed to the kinetically favored Zn−S bond dissociation. This reflects the small difference in the barriers for these two processes.

Overall, the kinetic and thermodynamic details of the insertion reaction favor the formation of **4**. This molecule contains a six-membered ring with P−O and Zn−O bonds, the latter of which are sites where reactions with additional molecules of **2** can occur. This will lead to the formation of long MP chains with a low proportion of metal atoms (see section III of the Supporting Information), assuming that the energetics are not altered significantly with each successive insertion. Additional constrained AIMD simulations in which **2** was replaced by $Zn(O_2PS)_2$, also a MTP derived from ZnDDPs,[10,23] showed that insertion occurred through a stepwise mechanism and led to the incorporation of metal atoms into the phosphate polymers, as shown in Figure 3. Static density functional theory calculations analogous to those described above indicated that the product of this reaction was most stable in the configuration indicated in Figure 3. This species contains a six-membered ring similar to that in **4**, as well as two four-membered rings originally present in the $Zn(O_2PS)_2$ reactant that contain Zn−O bonds. These bonds are potential sites for further insertion reactions to occur, which will allow for polymer growth to occur in several directions, leading to the formation of complex MP structures.

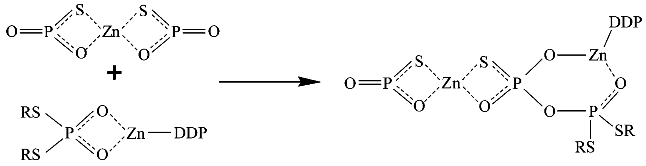

Figure 3. Insertion of $Zn(O_2PS)_2$ into **1**. R = methyl; DDP = $S_2P(OR)_2^-$.

In summary, we have performed a combined static and dynamic density functional theory study of the interaction between MTP and ZnDDP isomers. Although the motivation for these simulations stemmed from a need to understand how ZnDDPs are transformed into zinc phosphate antiwear films, it is clear that the results apply to other MP systems. The calculations led to the identification of a novel reaction involving the insertion of an MTP molecule into one of the Zn−O bonds in the ZnDDP isomer. This reaction was observed for two different types of MTP molecules and leads to the formation of complex MPs from relatively simple phosphate precursors. In fact, all of the "building blocks" considered in this study are produced through either the thermal decomposition or isomerization of ZnDDP molecules. As such, the observed reactions may shed light on chemical processes that occur during the transformation of ZnDDPs into MPs. Furthermore, it may be possible to control the decomposition of ZnDDPs and the subsequent formation of MPs through the selection of appropriate reaction conditions. Thus, the identified reaction has significant potential for use in the development of synthetic strategies directed toward the formation of MPs for use in various applications.

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Supporting Information Available: A full description of the calculations, details of all optimized structures, an envisioned polymerization mechanism, Figures S1 and S2, and a movie in AVI format demonstrating the insertion of **1** into **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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