A Quantum Chemical Study of the Unimolecular Decomposition Mechanisms of Zinc Dialkyldithiophosphate Antiwear Additives

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Received: February 11, 2004; In Final Form: May 6, 2004

Density functional theory calculations were applied to study a set of isomerization and decomposition reactions that zinc dialkyldithiophosphate (ZDDP) engine oil antiwear additives may take part in. The products of these reactions comprise a set of chemical species that can lead to the formation of poly(thio)phosphate films that are thought to be responsible for the antiwear protection offered by ZDDPs. The specific reactions examined involved either intramolecular alkyl group transfer within ZDDP or the intramolecular elimination of olefins from this molecule. A series of substituents were employed to examine how the nature of the substituent on the ZDDP molecule affects the thermodynamic and mechanistic details of these reactions, which in turns may have ramifications regarding various aspects of antiwear film formation. It was found that qualitative and quantitative aspects of these reactions were markedly different when hydrogen atoms were used as substituents instead of alkyl groups. The details of the reactions for the H-substituted system indicated that the precursors to the antiwear films should not be formed. When alkyl groups were employed as substituents, the energetic details of the reactions considered in this study exhibited a dependence upon the nature of these groups. An examination of these details revealed that straight-chained primary alkyl ZDDPs should decompose through reactions involving alkyl group transfer, while secondary and branched primary alkyl ZDDPs should primarily undergo olefin elimination reactions to form precursors to ZDDP antiwear films. The details of the reaction pathways that these systems follow to form the precursors shed light on the observed byproducts of antiwear film formation.

I. Introduction

The automobile engine presents a harsh environment under which surfaces are subjected to high loads and temperatures. Premature engine failure due to wear is rapid under such conditions if lubricants and antiwear additives are not used to protect the materials that form these surfaces. The most commonly used antiwear additives are zinc dialkyldithiophosphates (ZDDPs) which have the chemical formula $Zn[S_2P(OR)_2]_2$, where the label "R" represents an alkyl group.[1,2] The general structure of this molecule is shown in Figure 1.

ZDDPs were originally added to engine oils as antioxidants over 60 years ago; however, it was soon found that they were also highly effective antiwear agents.[3−5] Very little is known regarding the origin of the antiwear properties exhibited by ZDDPs, which is surprising in light of their longevity and universality as components in commercial engine oils. Recently, interest in the development of alternative antiwear additives has been driven by environmental concerns regarding the Zn, P, and S atoms of ZDDP[6,7] and by interest in the use of engines made of lightweight materials, such as aluminum, where the antiwear capabilities of ZDDPs are greatly diminished.[8,9] A clear understanding of the origin of the antiwear protection offered by ZDDP additives would be useful in the intelligent selection and design of alternative antiwear additives.

A great deal of experimental study has been directed toward understanding the nature of the antiwear properties exhibited by ZDDP additives.[1,2,10−14] It is generally accepted that these additives decompose under engine conditions, i.e., high temperatures and pressures, and that the decomposition products react to form a zinc poly(thio)phosophate film.[15−20] The exact chemical composition of the film is not known, and it is possible that a wide variety of films exist depending upon the specific conditions under which they are formed in the engine. The evolution of sulfur- and carbon-containing species such as olefins, sulfides, and mercaptans has also been observed to take place during the formation of ZDDP antiwear films,[21−24] and a number of mechanisms have been proposed to explain how the elimination of these volatile species from the system can lead to the formation of zinc poly(thio)phosphates.[16−18,20,21,23,25,26] Although none of these mechanisms have been proven to uniquely explain the formation of ZDDP antiwear films in a manner that is consistent with all of the available experimental data, the proposed mechanisms do share some common features that are potentially relevant to the formation of antiwear films. An examination of these processes at the atomic level may provide useful insight into the formation of ZDDP antiwear films.

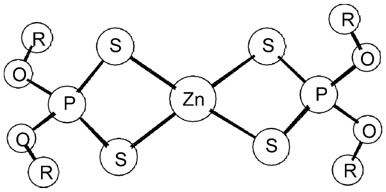

Figure 1. General structure of the ZDDP molecule. The label "R" denotes an alkyl group.

In general, the proposed mechanisms of ZDDP film formation follow the same pattern. First of all, the molecule either undergoes isomerization through the transfer of alkyl groups

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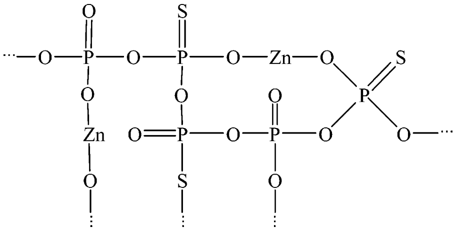


Figure 2. General structure of the antiwear film thought to be formed through the polymerization of the decomposition products of ZDDP antiwear additives. The bonding should continue in a rather random fashion to form an amorphous polyphosphate network.

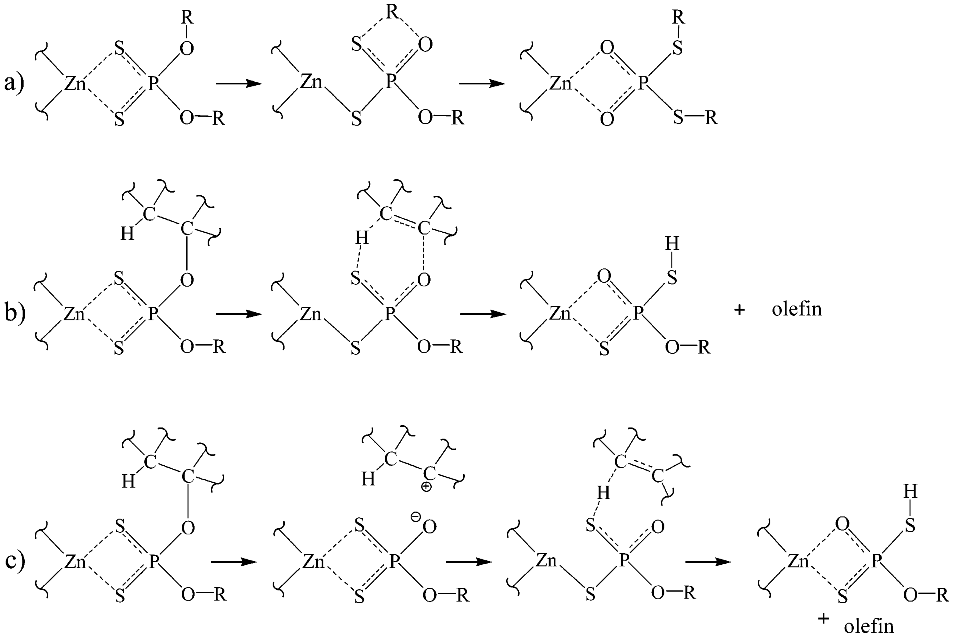
from the oxygen atoms to the sulfurs[16,17,21] or is partially decomposed through the elimination of alkyl groups in the form of olefins.[23,26] Further decomposition to remove some of the sulfur atoms as mercaptans and other sulfur-containing species then occurs along with or is followed by polymerization of the remaining phosphorus-containing species to form the (thio)-phosphate film.[16,17,21,23,26] This polymerization occurs through the formation of either P−O−P or P−S−P linkages between (thio)phosphate subunits, and an extensive amount of experimental evidence suggests that the product of the polymerization reaction is an amorphous zinc polyphosphate network with the occasional replacement of an oxygen atom by a sulfur.[15−20] An example of a structure consistent with this film is shown in Figure 2. The polymerization process requires both the elimination of substituents around the phosphorus to make that atom susceptible to nucleophilic attack and the removal of alkyl groups from the oxygen atoms to allow for their participation in linkage formation. The alkyl group transfer, olefin elimination, and sulfur elimination processes accomplish both of these objectives.

In some studies it has been suggested that film formation is dependent upon the interaction of ZDDP and its decomposition products with other chemical species that are present in the oil.[16−18,25,27] Some authors have also proposed that these reactions occur entirely after the ZDDP molecule has been adsorbed on and interacted with the surface material,[16,17] while in the other cases the role of the surface is not taken into consideration, and it is assumed that the film adheres to the surface at some stage during the overall process of film formation. Thus, it seems that, in a very general sense, the formation of ZDDP films involves three main steps, all of which may be affected by the presence of other chemical species in the oil including the engine surface. These processes, not necessarily in the order that they occur, are alkyl group transfer and elimination, leading to decomposition of the ZDDP molecule, polymerization of (thio)phosphate subunits, and the adsorption of ZDDP or its decomposition products on the antiwear film on the surface.

Although it would appear that the main steps involved in the formation of ZDDP antiwear films have been identified, this is only true on a very general level, and a great deal of uncertainty exists regarding the specific details of the processes leading to film formation. For example, the atomic-level details of the chemical reactions leading to the decomposition of the ZDDP molecule are not entirely known and thus have not been examined in detail. Other aspects of ZDDP additives and films that remain unclear include the effect of other chemical species on the decomposition of ZDDP and formation of antiwear films, the role of the surface in antiwear film formation, and the atomic-level details of the film responsible for the observed antiwear properties. These uncertainties arise from a multitude of difficulties associated with the experimental study of ZDDP antiwear additives and films. These include the difficulty in obtaining atomic-level details regarding chemical processes through experiment, the fact that the conditions under which ZDDP films are formed in the engine are not amenable to experimental study, the likelihood that different film formation mechanisms are operational under different conditions which, in turn, leads to the formation of different films, and the fact that most experiments focus on the characterization of the antiwear films rather than on the atomic-level details of the formation and properties of the films. The development of a complete understanding of the formation, behavior, and properties of ZDDP antiwear films, which would aid in the design of effective alternative antiwear additives, has been severely hampered by these issues, and it is clear that alternative methods must be employed to obtain additional information pertaining to ZDDP additives and films.

Computational simulation has proven to be an effective means of developing a clear description of the atomic-level details of chemical processes through the calculation of molecular structures and energetics. Simulations at various levels of theory have previously been employed to examine the structural aspects of ZDDP molecules in monomeric, dimeric, and isomeric forms.[28−30] The reactivity of various atomic centers within the ZDDP molecule toward O^{2-} anions, to model the interaction with an oxide surface, has also been examined with semiempirical molecular orbital methods;[31] however, the results of that study are questionable given that the representation of the surface with a single anion is clearly inadequate. In other studies the properties of a model for the antiwear film comprised of a monolayer of dialkyldithiophosphate (DDP) ions, and dithiocarbamate model antiwear additives, adsorbed on an iron oxide surface were examined with molecular mechanics techniques.[32,33] In those studies, it was found that the binding energy of the DDP ion on the oxide surface exhibited a dependence upon the nature of the alkyl substituent on the DDP ion that was analogous to the observed trend in the antiwear capabilities of films derived from ZDDPs with different substituents. On the basis of this similarity, it was proposed that the antiwear effectiveness of ZDDPs with different alkyl substituents was dependent upon the magnitude of the binding energy between the DDP anion and the iron oxide surface. Although the results of those studies seem to provide insight into some of the basic atomic-level details related to ZDDP antiwear films, the methods and model systems used are debatable, particularly when considering that a great deal of experimental evidence suggests that antiwear films are multilayered polyphosphate structures as opposed to a monolayer of DDP ions.[15−20] More recently, ab initio molecular dynamics simulations have been used to study the finite temperature behavior of ZDDP antiwear additives with a variety of alkyl substituents.[28] In that study it was observed that the ZDDP molecule can decompose through several routes involving the elimination of olefins, sulfides, and radicals, which is consistent with experimental observations regarding the decomposition of these additives. Furthermore, the results of that study shed light on differences in the behavior of ZDDPs with aliphatic and aryl substituents that could be correlated with the observed differences in the antiwear properties of films derived from these types of additives. The results of that study are more reliable than those of the earlier studies since high-level simulation methods were used and minimal assumptions were made regarding the model systems under study. Thus, it is clear that meaningful results can be obtained through simulation as long as care is taken in the selection of the method and model systems used, and it is unfortunate that

SCHEME 1: Mechanisms for the Reactions Considered in This Study: (a) Alkyl Group Transfer, (b) Concerted Olefin Elimination, and (c) Stepwise Olefin Elimination[a]



[a] Portions of the molecules have been removed for clarity. The products shown correspond to the final products of the reaction and may not be the direct products following the transition state. This point is discussed further in the main text.

more theoretical studies of ZDDP additives and films have not been reported.

In the current study the mechanistic and thermodynamic details of the alkyl group transfer and olefin elimination processes leading to the isomerization and decomposition of the ZDDP molecule will be examined with quantum chemical methods. The polymerization and adsorption processes involved in ZDDP antiwear film formation will be examined in future studies. Furthermore, in the current work only intramolecular reactions leading to alkyl group transfer and olefin elimination will be explicitly considered despite the fact that it has been proposed that alkyl group transfer may take place through bimolecular reactions involving other ZDDP molecules[21] or basic species present in the oil.[34] The investigation of such bimolecular processes will be presented in a separate study. The results of the current investigation will provide fundamental atomic-level insight into the processes of isomerization and decomposition of the ZDDP molecule that will aid in the development of a clear description of the steps leading to the formation of antiwear films.

The specific mechanisms that will be considered in this study are outlined in Scheme 1. The mechanism labeled “a” corresponds to the intramolecular transfer of an alkyl group from an oxygen atom to an adjacent sulfur atom. Previous experimental[23,26] and theoretical[28] studies have provided evidence suggesting that olefin elimination occurs through the transfer of a β-hydrogen atom from one of the alkyl groups to a sulfur atom through either of the mechanisms labeled “b” and “c” in Scheme 1. In the mechanism labeled “b” the reaction occurs in a concerted manner while “c” takes place in a stepwise fashion involving initial formation of a carbonium ion followed by β-hydrogen transfer.

It is known that ZDDP additives with different types of alkyl groups exhibit differences in both the rates and byproducts of film formation[21,22] as well as in the antiwear capabilities of the resulting film.[35−37] It has been shown that antiwear film formation occurs fastest for secondary alkyl ZDDPs, is slower for straight-chained primary alkyl ZDDPs, and is slowest for branched primary alkyl ZDDPs.[21,22] The byproducts of straight-chained primary alkyl ZDDPs are mainly composed of dialkyl sulfides, while those produced from branched primary and secondary alkyl ZDDPs contain large quantities of H_2S gas.[21,22] Additionally, it is known that films derived from secondary alkyl ZDDPs exhibit antiwear properties that are superior to those of primary alkyl ZDDPs and that ZDDPs with aryl groups as substituents yield films of very low quality.[35−37] Since these differences in various aspects of the formation and properties of antiwear films exhibit a dependence upon the nature of the alkyl group, it is possible that they are due to fundamental details of the reactions considered in this study, which explicitly involve the alkyl groups and are thought to occur experimentally. In this study calculations will be performed on ZDDP molecules with a series of substituents in order to examine how various aspects of these reaction differ for different types of ZDDPs. In particular, this study will focus on the identification of precursors to the antiwear films for ZDDPs with different types alkyl groups. The study of the effect of the nature of the alkyl group on the rate of film formation and quality of the antiwear film requires knowledge of the mechanism of film formation and will be examined in future studies of how the precursors identified in the current work can react to yield antiwear films.

Thus, the overall goal of this study is to examine the intramolecular alkyl group transfer and olefin elimination reactions that ZDDPs take part in through chemical simulation. This information will be used in an effort to identify the potential precursors to ZDDP antiwear films for additives with different types of alkyl groups, which in turn will be used in future studies of the formation of antiwear films. The computational methods and model systems that were used are described in the next section. This is followed in section III by a detailed discussion of the energetic and mechanistic details of the alkyl group transfer and olefin elimination reactions and an investigation of their relationship to the overall process of antiwear film formation. The conclusions are given in section IV.

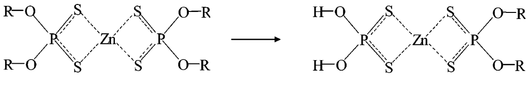
II. Computational Details

a. Methods. Kohn−Sham density functional theory[38,39] (DFT) was used for the calculation of the energies and structures of all reactants, products, intermediates, and transition states reported in this study. These calculations were all performed with the Jaguar 5.0 software package.[40] Becke's three-parameter hybrid gradient-corrected exchange functional[41] was used in conjunction with the gradient-corrected correlation functional of Lee, Yang, and Parr,[42] which is commonly referred to as the B3LYP functional. A 6-31+G(d,p) basis set was used on all atoms except zinc, which was treated with the LAV3P effective core potential (ECP),[43] where the naming of the ECP is consistent with that used in the Jaguar 5.0 manual. In this ECP the 3d and 4s electrons of the zinc atom are treated with the 6-31G basis set, and the remaining electrons are treated with an ECP of the variety developed at Los Alomos National Laboratories.

Frequency calculations were performed on all stationary points to confirm that all minima possessed no imaginary frequencies and that all transition states possessed only one. Unscaled zero-point vibrational energy corrections (ZPVE) are included in all reported energies. The transition states were characterized through a visual examination of the normal mode with the imaginary frequency. Intrinsic reaction coordinate calculations were not performed since that option is not available in Jaguar 5.0.

ZDDP additives react and decompose under high-temperature conditions within the engine, and hence it may be of interest to estimate the effect of temperature on the relative energetics along the located reaction pathways. The free energies of the stationary points along these pathways were calculated during the frequency calculations within the ideal gas approximation at 1 atm and temperatures of 300 and 500 K and are reported along with the electronic energies. These particular temperatures were selected since 300 K roughly corresponds to room temperature and 500 K approximates both the average surface temperature of running engines where film formation takes place[44] and the temperatures often used to thermally initiate antiwear film formation.[16,17] The ZDDP molecules and the species derived from them possess several very low frequencies which may introduce significant errors into the calculation of the molecular entropies and free energies. To minimize these errors, all normal modes with frequencies of less than 100 cm^{-1} were excluded from the free energy calculations. The natural bond order (NBO) program[45] distributed with Jaguar 5.0 was used for the calculation of all Wiberg bond orders[46] and NBO charges[47,48] reported in this study.

Since the alkyl groups on the ZDDP molecule and its derivatives may adopt a large number of conformations, a systematic scheme was used in an effort to locate a global minimum when optimizing the structures of the reactants and products. Within this geometry optimization scheme a 1.0 ns molecular dynamics simulation was performed at 1000 K using the Universal 1.02 force field[49,50] with the Cerius2 molecular modeling package.[51] One hundred structures were selected at regular intervals along the resulting trajectory and optimized at the PM3 semiempirical level of theory[52,53] with the Gaussian 98 suite of programs.[54] The 10 unique lowest energy structures were then optimized with DFT methods as described above, and the data corresponding to the lowest energy DFT structure are reported in what follows. This procedure does not guarantee the location of a global minimum; however, it does allow for the consideration of a large number of structures in an automated fashion which should remove the errors that would likely be introduced by assuming that one particular conformation is the most stable. The transition-state geometries were based on those of the reactants, and the optimization scheme outlined above was not used.



Full ZDDP Model ZDDP

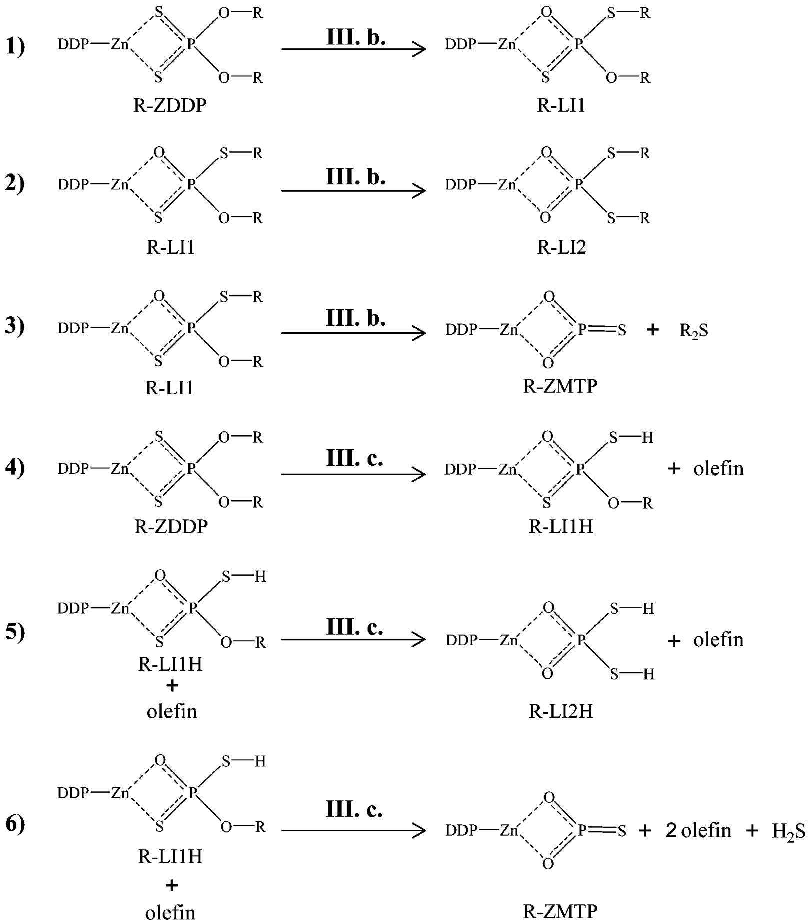
Figure 3. Comparison of the parent and model ZDDP systems. The model system is derived from the fully substituted molecule by replacing the alkyl groups in one of the DDP ligands with hydrogen atoms. All reactions considered in this study take place within the DDP group that has not been modified.

b. Model Systems. As mentioned above, one of the goals of this study is to examine the effect of different substituents on the energetic and mechanistic details of the intramolecular reactions under consideration. A series of model compounds with different substituents were employed in order to achieve this goal. The specific substituents considered were hydrogen (H), ethyl (Et), isopropyl (^{i}Pr), and isobutyl (^{i}Bu) groups which allow for a comparison to be made between straight-chained primary (Et), secondary (^{i}Pr), and branched primary (^{i}Bu) alkyl ZDDPs. The H-substituted case provides an example where the electronic and steric effects of the substituents are minimal. Although experimental evidence suggests that aryl-substituted ZDDPs yield antiwear films of very poor quality,[35−37] these substituents were not considered in this study since they are unlikely to take part in alkyl group transfer and olefin elimination through the mechanisms outlined in Scheme 1. Furthermore, the results of previous simulations have shown that aryl-substituted ZDDPs primarily decompose through the elimination of alkoxy radicals, while other decomposition pathways, including olefin elimination, are available for alkyl-substituted ZDDPs.[28] In that study it was also found that ZDDPs with nonaryl substituents can decompose through the elimination of alkyl radicals; however, since the energetics of this process were examined in that study, they will not be considered again here. Tertiary alkyl substituents will not be considered in this study since they are not used experimentally due to their instability.

The consideration of increasingly larger substituents quickly leads to an increase in the size of the system and the computational effort required to perform the calculations. This is due to the fact that the ZDDP molecule contains four identical alkyl groups, and hence increasing the size of the alkyl substituent through the addition of a methyl group, i.e., going from ethyl to isopropyl groups, actually places four extra methyl groups on the ZDDP molecule as a whole. Since the reactions considered here involve only one DDP group at a time, it may only be necessary to change the alkyl substituents within the DDP group that is involved in the reaction while using smaller substituents on the DDP ligand that is not participating in the reaction. In this study model systems were used in which the reacting DDP ligand was substituted by one of the alkyl groups in the series given above while the other DDP group was substituted by hydrogen atoms. The relationship between the true and model system for a given type of alkyl substituent is shown in Figure 3.

Calculations were performed on the stationary points, i.e., minima and transition states, along the pathways for the three intramolecular alkyl group transfer reactions, labeled **1** to **3** in Scheme 2, for both the fully substituted ethyl−ZDDP system and the corresponding model system to investigate whether any substantial errors were introduced through the use of the smaller model systems. The results of these calculations showed that

SCHEME 2: Reactions Considered in This Study[a]



[a] The labels underneath each of the phosphorus-containing apecies are explained in the main text. The labels over the arrows indicate in which sections of the discussion the various mechanisms for these reactions can be found.

the largest difference in the thermodynamic values for any of these reactions was 1.3 kcal/mol, the largest difference in any of the barriers was 1.6 kcal/mol, and all bond lengths agreed within at least 0.10 Å. The agreement is quite good and indicates that the use of the smaller model systems will not likely provide misleading results.

III. Results and Discussion

The results of calculations on the reactants and products of the reactions considered in this study are given in part a. This is followed by a discussion of the mechanism for the intramolecular alkyl group transfer in part b and of the mechanism for olefin elimination in part c. In part d the mechanistic and thermodynamic details are summarized and used to determine the reaction pathways that lead to the formation of precursors to the ZDDP antiwear films for additives with different alkyl substituents.

a. Thermodynamics of the Alkyl Group Transfer and Olefin Elimination Reactions. Each DDP ligand contains two alkyl groups that can be transferred or participate in olefin elimination, and hence the reactions considered here can occur twice within a single DDP group. A full set of reactions that allows for two consecutive alkyl group transfer or olefin elimination reactions to take place within a single DDP group was developed and used as the basis for the calculations in this study. These reactions are shown in Scheme 2. For the sake of simplicity it is assumed that each DDP group exclusively participates in either alkyl transfer or olefin elimination. That is, the case where alkyl group transfer is followed by olefin elimination, or vice versa, is not explicitly considered; however, it is noted that such combinations of reactions are possible. The products of the reactions shown in Scheme 2 are important within the context of ZDDP antiwear film formation since they are known to be formed experimentally[16,17,21−23] and have properties consistent with precursors to the antiwear films.

The unconventional two part naming format indicated in Scheme 2 will be used to identify the phosphorus-containing species. The first part of a particular name will identify the type of substituent that was present on the parent ZDDP molecule. As noted above, the labels H, Et, ^{i}Pr, and ^{i}Bu will be used to denote the hydrogen, ethyl, isopropyl, and isobutyl species, respectively. The second part of the name will indicate the chemical nature of the structure. In reaction 1 the system starts in the ZDDP form, referred to as R-ZDDP, where R is the appropriate substituent label, and undergoes the transfer of one alkyl group to form what is called a linkage isomer. This isomer is denoted as R-LI1, where the LI1 term indicates that this is a linkage isomer formed through the transfer of one alkyl group from an oxygen atom to a sulfur. In reaction 2 the system starts in the R-LI1 form, and a second alkyl group is transferred to the sulfur atom that is not alkylated. The product of this reaction is referred to as R-LI2, since it is the linkage isomer formed through a second alkyl group transfer. Reaction 3 also starts with the species in the R-LI1 form and involves the transfer of a second alkyl group; however, in this case the alkyl group is transferred to the alkylated sulfur atom to form a dialkyl sulfide and a zinc metathiophosphate. This product will be denoted as R-ZMTP; however, it should be noted that for the Et-, ^{i}Pr-, and

TABLE 1: Electronic and Free Energies[a] of the Products of Reactions 1−6 Relative to the Appropriate Parent ZDDP Molecule

reaction[b]	products[c]	E_{rel}	$G_{rel}(300)^d$	$G_{rel}(500)^d$
	H			
1	H-LI1	1.4	1.3	1.3
2	H-LI2	5.6	5.7	5.8
3	H-ZMTP + H_2S	22.9	11.7	3.4
	Et			
1	Et-LI1	−1.8	−2.4	−3.3
2	Et-LI2	−1.9	−2.8	−4.4
3	Et-ZMTP + Et_2S	17.6	1.7	−10.7
4	Et-LI1H + C_2H_4	16.9	4.4	−5.5
5	Et-LI2H + $2C_2H_4$	34.0	9.1	−11.0
6	Et-ZMTP + $2C_2H_4$ + H_2S	51.2	15.1	−13.3
	^{i}Pr			
1	^{i}Pr-LI1	−0.2	−0.8	−1.8
2	^{i}Pr-LI2	2.7	2.5	2.3
3	^{i}Pr-ZMTP + $^{i}Pr_2S$	22.0	5.1	−7.9
4	^{i}Pr-LI1H + C_3H_6	15.7	0.6	−11.2
5	^{i}Pr-LI2H + $2C_3H_6$	32.7	3.7	−18.8
6	^{i}Pr-ZMTP + $2C_3H_6$ + H_2S	50.0	9.7	−21.1
	^{i}Bu			
1	^{i}Bu-LI1	−1.1	−0.2	−0.2
2	^{i}Bu-LI2	−1.8	0.1	1.9
3	^{i}Bu-ZMTP + $^{i}Bu_2S$	18.1	2.4	−9.4
4	^{i}Bu-LI1H + i-C_4H_8	10.3	−4.1	−15.5
5	^{i}Bu-LI2H + 2i-C_4H_8	20.7	−8.6	−31.8
6	^{i}Bu-ZMTP + 2i-C_4H_8 + H_2S	38.0	−2.6	−34.1

[a] Energies are in kcal/mol relative to the parent ZDDP molecule and include ZPVE corrections. [b] The numbers identifying the reactions correspond to those given in Scheme 2. [c] The products are those indicated in Scheme 2 for each of reactions 1−6. [d] The temperatures in kelvin are indicated in parentheses.

^{i}Bu-substituted systems the R-ZMTP species is identical to H-ZMTP since the unreacted DDP group in the model species has hydrogen atoms as substituents.

Reaction 4 is the first olefin elimination from the ZDDP molecule and results in the formation of a phosphorus-containing species that is similar to R-LI1, except that a hydrogen atom is bonded to the sulfur instead of an alkyl group. This species will be referred to as R-LI1H due to the similarity with R-LI1, where the "H" indicates that a hydrogen atom is present on the sulfur. It is possible for further olefin elimination from R-LI1H to take place in either of two ways. In reaction 5 the olefin elimination occurs with a β-hydrogen being transferred to the sulfur atom that does not have a hydrogen substituent while in reaction 6 the hydrogen atom is transferred to the sulfur that has a hydrogen atom bonded to it. For the Et-, ^{i}Pr-, and ^{i}Bu-substituted species the phosphorus-containing product of reaction 5 is actually identical to H-LI2; however, to distinguish this product as being formed through olefin elimination, it will be denoted as R-LI2H. The phosphorus-containing product of reaction 6 is identical to the R-ZMTP species for each of these systems and will be identified with the same name.

The electronic and free energies of the products of the reactions outlined in Scheme 2 are given relative to the energy of the parent ZDDP molecule in Table 1. The reader is cautioned that the values in this table are not the reaction energies for each of these reactions. The energetics for the transition state and intermediate structures along the possible pathways for these reactions can be found in the sections of the discussion that are indicated by the labels above the arrows in Scheme 2.

It is apparent from the data in Table 1 that the energetic values for the H-substituted species are markedly different than those calculated for the alkyl-substituted ZDDPs. The electronic and free energies indicate that H-ZDDP is more stable than its isomers or decomposition products at all temperatures. On the other hand, the data for all of the alkyl-substituted systems indicate that at least one species other than the parent ZDDP molecule is thermodynamically favored at all temperatures. The differences between the H- and alkyl-substituted systems call into question the validity of using hydrogen atoms as substituents in the DDP groups that are taking part in the reactions since the results with these substituents are both qualitatively and quantitatively different than those obtained through calculations on ZDDPs with alkyl substituents to a significant extent.

The relative electronic energies (ΔE) in Table 1 indicate that R-LI2 is the most stable species for the Et- and ^{i}Bu-substituted systems and that ^{i}Pr-LI1 is the most stable of the ^{i}Pr-substituted species. When temperature effects are not considered, it is also clear that the products formed through the dissociation reactions (numbered 3−6) are all thermodynamically disfavored. These results indicate that, with the exception of H-ZDDP, the ZDDP molecule is not actually stable with respect to at least one of its isomers. This is consistent with the results of our previous calculations on R-ZDDP and R-LI1 molecules with a series of alkyl substituents similar to that used here.[28]

The relative thermodynamic stabilities of the products of the reactions considered here are particularly relevant at 300 K since oil, which contains ZDDP, spends long periods of time at temperatures of ∼300 K in containers and in automobiles that are not running and have sufficiently cooled. These long-standing periods decrease the importance of kinetic considerations at this temperature, at least for reversible reactions, and instead the relative thermodynamic stabilities of the products are relevant with respect to the structure of ZDDP molecules at room temperature. At 300 K the effect of temperature on the relative energetics of reactions 1 and 2 is minimal, and for all substituents the relative free energies at this temperature are nearly the same as the relative electronic energies. This is not surprising since R-ZDDP, R-LI1, and R-LI2 have similar entropy values, and hence the relative free energies are not greatly dependent upon the temperature. On the other hand, the relative energies of reactions 3−6 all exhibit a significant decrease when temperature effects are considered due to the fact that all of these reactions involve the dissociation of the ZDDP molecule and are entropically favored at finite temperature. At 300 K, there is already a clear difference between the behavior of the branched primary alkyl-substituted system (^{i}Bu-ZDDP) and the other two alkyl-substituted systems. The thermodynamic data for the Et- and ^{i}Pr-substituted systems favor the formation of isomers at this temperature while the ^{i}Bu-ZDDP system is most stable as ^{i}Bu-LI2H. The increased stability of the products of the olefin elimination reactions for the ^{i}Bu-substituted system is likely due to the fact that the C−C double bond in the isobutene product is stabilized by substituent effects to a greater degree than in the corresponding alkene product for the Et- and ^{i}Pr-substituted systems.

The free energy data at 500 K, which is similar to average engine surface temperatures, show that the reactions leading to dissociation (numbered 3−6) are favored over those that do not involve dissociation (reactions 1 and 2). In all cases the products of reaction 6 are the most stable at this temperature. The fact that the decomposition products are favored at higher temperatures is not surprising since the higher entropy of the dissociated species will act to decrease the relative free energies as the temperature is increased. The results also show that the products of the olefin elimination reactions (4−6) become increasingly favored as the number of carbon atoms in the alkyl group is increased. Once again, this is consistent with the increased stabilization of the C−C double bond in the olefin product as the size of the alkyl group is increased for the substituents used here.

Thus, the thermodynamic data demonstrate that both temperature and substituent effects exist for the alkyl group transfer and olefin elimination reactions. These effects will result in differences in the reaction pathways that different types of ZDDPs follow during the formation of precursors to the antiwear films. The elucidation of such pathways will take place in part d of the discussion.

b. The Mechanism of Intramolecular Alkyl Group Transfer. As mentioned above, experimental evidence suggests that alkyl group transfer within the ZDDP molecule is a key step in the formation of ZDDP antiwear films.[16,21] Although it has been suggested that the alkyl groups may be transferred through bimolecular reactions,[21,34] in this study only an intramolecular mechanism will be considered. This mechanism is labeled “a” in Scheme 1 and involves the direct transfer of an alkyl group from one of the oxygen atoms to an adjacent sulfur atom within the same DDP ligand. In Scheme 1 the mechanism was explicitly drawn for the reaction starting from the parent ZDDP molecule which leads to the formation of R-LI1 as outlined in reaction 1 in Scheme 2. As noted above, R-LI1 can undergo further alkyl group transfer to yield either R-LI2 or R-ZMTP and R_2S as in reactions 2 and 3, respectively. In this part of the discussion the mechanisms of alkyl group transfer will be examined for all three of these reactions. The naming convention for the transition-state structures will be an extension of that used to describe the reactants and products. Each transition-state structure will be given a three-part name where the first part identifies the alkyl substituent on the parent ZDDP, the second part denotes the phosphorus-containing product of the reaction, and the third part is the label ATS‡ which indicates that this is an alkyl group transfer transition state. The third part of this naming scheme is necessary to distinguish these transition states from those that will be discussed in the next section which also have the same first two labels. Thus, the transition states for reactions 1, 2, and 3 are labeled as R-LI1-ATS‡, R-LI2-ATS‡, and R-ZMTP-ATS‡, respectively.

Three intermediate structures were located along these pathways corresponding to the direct product following each of the transition states. Structural details of these intermediates are given in Figure 4. The intermediate along the pathway for reaction 1 following the formation of R-LI1-ATS‡ is a structure in which the zinc is still coordinated by the two sulfur atoms in the DDP ligand where isomerization has occurred; however, one of the sulfurs has an alkyl substituent. This structure is referred to as R-LI1a. Similarly, the direct product from the transition state in reaction 2 is a structure in which the DDP ligand taking part in the reaction is coordinated to the zinc through a dealkylated oxygen atom and an alkylated sulfur atom. This structure will be referred to as R-LI2a. An intermediate complex in which the R_2S molecule is weakly bound to R-ZMTP was located along the pathway for reaction 3 and will be referred to as R-ZMTPa. In this complex the zinc atom of the R-ZMTP component is substituted by three sulfurs and one oxygen and the phosphorus atom of the DDP group that has participated in dissociation is weakly coordinated by the sulfur atom of the R_2S molecule. In the product the zinc atom in R-ZMTP is coordinated by two sulfurs (undecomposed DDP ligand) and two oxygens (decomposed DDP ligand), and R_2S has been removed from the system.

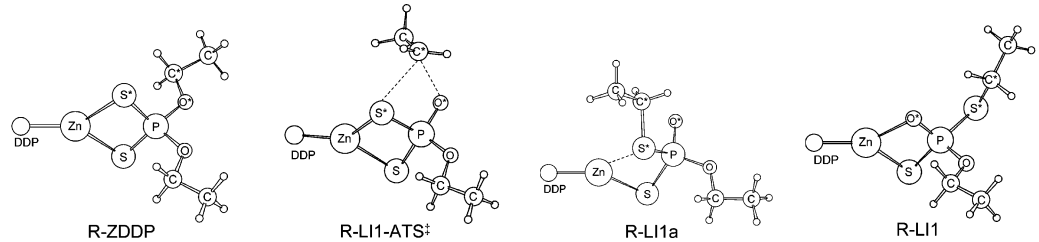
The energies of the intermediate structures along the reaction pathways were calculated, but the location of the transition states linking these structures to the R-LI1, R-LI2, and R-ZMTP products was not attempted. The reason for this is that once the system proceeds past the transition state, the alkyl group has already been transferred, and the difference between the intermediate and the final product is primarily due to the coordination at the zinc atom. In a previous theoretical study[28] it was shown that the coordination at this atom readily fluctuates at finite temperature, and hence it is unlikely that the transition states for the interconversion of the intermediate to the final product are important with respect to the isomerization or decomposition of the ZDDP molecule.

The electronic and free energies of the reactants, products, intermediates, and transition states for the three alkyl group transfer reactions considered here were calculated and are provided in Table 2. Selected geometric data for the stationary points along the reaction pathways for each of reactions 1−3 are given in Figure 4. Specific details regarding the electronic structures of the stationary points along the reaction pathways are given throughout the discussion as appropriate, and full details are provided in Table 1S of the Supporting Information.

Reaction 1 involves the progression from R-ZDDP through the R-LI1-ATS‡ transition state to yield R-LI1 as shown in Scheme 1a. In the H-LI1-ATS‡ transition state the O−H bond distance has increased to 1.414 Å from its original value of 0.969 Å in the reactant ZDDP while the S−H bond distance has decreased to 1.579 Å, which is only slightly longer than its respective value of 1.352 Å in H-LI1. These bond lengths are consistent with a process where the dissociation of the O−H bond and the formation of the S−H bond occur in a concerted fashion as in the mechanism labeled “a” in Scheme 1. An examination of the electronic structure of the transition state supports this interpretation. For example, the O−H and S−H Wiberg bond orders[46] were found to be 0.25 and 0.60, respectively, and it was observed that the NBO charge[47,48] on the hydrogen atom that was transferred decreased from $+0.550e$ in the reactant to $+0.345e$ in the transition state. These data indicates that substantial bonding between the hydrogen atom and the remainder of the ZDDP molecule exists throughout the reaction.

In the H-LI1a intermediate the hydrogenated sulfur is still coordinated to the zinc atom. This is apparent through the Zn−S distance which has only increased slightly to 2.624 Å from its original value of 2.456 Å in the reactant H-ZDDP. The S−H bond is fully formed in the intermediate as evidenced by the bond order of 0.94, which indicates that the transfer process has completed at this point along the reaction pathway. The formation of this bond leads to a decrease in the P−S bond order from 0.91 in the transition state to 0.73 in the intermediate. The P−O bond order has increased to 1.29 in this structure from 0.99 in the transition state which indicates that the interaction between these two atoms has increased in the intermediate. In the final product, H-LI1, the Zn−S bond has dissociated and the P−S bond order has increased to 0.96 while the Zn−O distance has decreased to 2.069 Å as that bond is formed.

The calculations on the alkyl-substituted systems indicated that alkyl group transfer within these molecules occurs through a different mechanism than that observed for the H-substituted system. The initial indication of this difference is found in the structural details of the transition states where the C−O distance has been extended by at least 0.8 Å relative to the same distance in the corresponding R-ZDDP molecule for the alkyl-substituted systems while for the H-substituted system this increase was much less pronounced. For all alkyl-substituted ZDDPs it was also observed that the total charge on the alkyl groups being



R-ZDDP

R	Zn-S*	S*-C*	C*-O*
H	2.456	3.038	0.969
Et	2.444	3.584	1.454
^{i}Pr	2.439	3.592	1.471
^{i}Bu	2.442	3.588	1.455

R-LI1-ATS‡

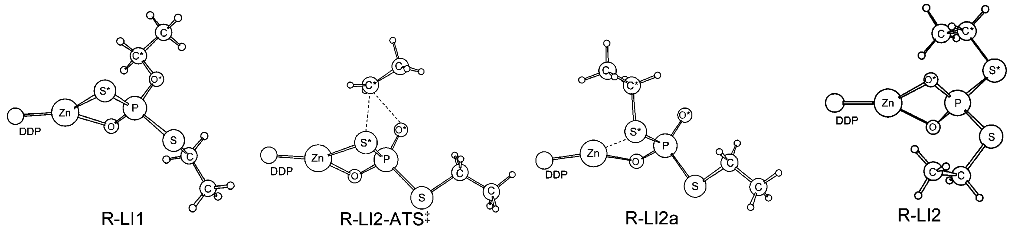
R	Zn-S*	S*-C*	C*-O*
H	2.551	1.579	1.414
Et	2.498	2.846	2.335
^{i}Pr	2.432	3.042	2.590
^{i}Bu	2.453	2.953	2.391

R-LI1a

R	Zn-S*	S*-C*	C*-O*
H	2.624	1.349	2.799
Et	2.581	1.856	3.138
^{i}Pr	2.563	1.876	3.162
^{i}Bu	2.566	1.858	3.153

R-LI1

R	Zn-S*	S*-C*	C*-O*
H	2.069	1.352	3.168
Et	2.069	1.862	3.284
^{i}Pr	2.069	1.882	3.261
^{i}Bu	2.069	1.864	3.598



R-LI1

R	Zn-S*	S*-C*	C*-O*
H	2.484	3.414	0.972
Et	2.459	3.689	1.461
^{i}Pr	2.453	3.680	1.476
^{i}Bu	2.454	3.716	1.462

R-LI2-ATS‡

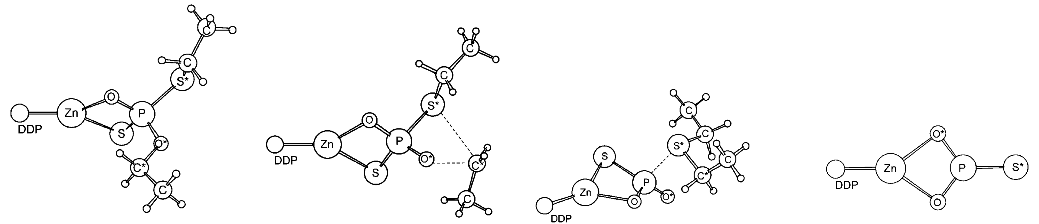
R	Zn-S*	S*-C*	C*-O*
H	2.552	1.587	1.409
Et	2.465	2.880	2.344
^{i}Pr	2.422	3.046	2.590
^{i}Bu	2.451	2.953	2.387

R-LI2a

R	Zn-S*	S*-C*	C*-O*
H	2.608	1.348	2.828
Et	2.587	1.859	3.178
^{i}Pr	2.526	1.885	3.344
^{i}Bu	2.542	1.861	3.196

R-LI2

R	Zn-O*	S*-C*	C*-O*
H	2.106	1.349	3.143
Et	2.076	1.859	3.094
^{i}Pr	2.079	1.883	3.163
^{i}Bu	2.077	1.861	3.067



R-LI1

R	P-S*	S*-C*	C*-O*
H	2.111	3.790	0.972
Et	2.101	4.329	1.461
^{i}Pr	2.103	4.372	1.476
^{i}Bu	2.104	4.330	1.462

R-ZMTP-ATS‡

R	P-S*	S*-C*	C*-O*
H	2.442	1.546	1.398
Et	2.203	2.865	2.380
^{i}Pr	2.206	3.080	2.578
^{i}Bu	2.204	2.888	2.457

R-ZMTPa

R	P-S*	S*-C*	C*-O*
H	2.811	1.348	3.321
Et	2.456	1.839	3.177
^{i}Pr	2.465	1.871	3.316
^{i}Bu	2.423	1.840	3.253

R-ZMTP

R	Zn-O*	P-O*	P-S*
H	2.112	1.538	1.906
Et	2.112	1.538	1.906
^{i}Pr	2.112	1.538	1.906
^{i}Bu	2.112	1.538	1.906

Figure 4. Structures and relevant bond distances for the stationary points along the reaction pathways for reactions 1−3. Note that the structures shown all correspond to the Et-substituted species. The bond lengths given below each structure are in Å. For the H-substituted compounds the terms S*−C* and C*−O* refer to S*−H* and H*−O*, respectively, where H* is the hydrogen atom that is being transferred from the oxygen to the sulfur. Note that the unreacted DDP group has been replaced with the generic symbol DDP.

transferred increased by +0.208*e*, +0.323*e*, and +0.209*e* for the Et-, ^{i}Pr-, and ^{i}Bu-substituted systems, respectively, as the system proceeded from the reactants to the transition state. For the Et- and ^{i}Bu-substituted transition states the C−O bond order was ∼0.25 while for ^{i}Pr-LI1-ATS‡ this value was 0.09. The bond orders between the sulfur atom and the α-carbon of the alkyl group vary from 0.24 to 0.34 in the transition state which indicates that this bond is not formed to the same degree as the O−H bond in the H-LI1-ATS‡. These results are consistent with the transfer of the alkyl group in an asynchronous fashion where the C−O bond has undergone significant dissociation before the C−S bond has formed to a substantial degree. The observed increase in the charge on the alkyl group that is being transferred during this process is due to a combination of the heterolytic cleavage of the C−O bond and the asynchronicity of the bond formation and dissociation during the reaction. The fact that no additional intermediate structures were located between R-LI1-ATS‡ and R-LI1a indicates that the alkyl transfer occurs in a concerted manner; however, the formation and dissociation of the S−C and O−C bonds do not occur in unison.

For all of the alkyl substituents the R-LI1a intermediates were similar to the analogous species for the H-substituted system. The Zn−S bond lengths were slightly increased to values ranging from 2.563 to 2.590 Å, depending upon the substituent, which indicates that interaction between the zinc and sulfur atom is still present. The S−C bond orders were all approximately 1.00 in the intermediate which demonstrates that the alkyl group transfer has been completed at this point along the reaction coordinate. The P−S bond orders also experienced a decrease from values of ∼0.95 in the transition state to ∼0.75 in the intermediate which is a result of the formation of the S−C bond. The P−O bond order also increases as the system moves from the transition state to the intermediate and then decreases in the final product as the Zn−O bond is formed. Overall, the fact that the intermediates and products for the alkyl- and H-substituted systems are similar indicates that the main difference

TABLE 2: Relative Electronic and Free Energies[a] of the Stationary Points along the Pathways for the Alkyl Group Transfer Reactions 1−3 within the H-, Et-, ^{i}Pr-, and ^{i}Bu-Substituted ZDDPs Molecules

reaction[b]	species[c]	Δ*E*	Δ*G*(300)[d]	Δ*G*(500)[d]
	H			
1	H-ZDDP	0.0	0.0	0.0
	H-LI1-ATS‡	32.7	33.1	33.8
	H-LI1a	14.1	14.2	14.3
	H-LI1	1.4	1.3	1.3
2	H-LI1	0.0	0.0	0.0
	H-LI2-ATS‡	31.7	31.5	31.3
	H-LI2a	12.2	12.3	12.2
	H-LI2	4.2	4.4	4.5
3	H-LI1	1.4	1.3	1.3
	H-ZMTP-ATS‡	33.9	34.1	34.6
	H-ZMTPa	20.5	20.8	22.1
	H-ZMTP + H_2S	21.5	10.4	2.1
	Et			
1	Et-ZDDP	0.0	0.0	0.0
	Et-LI1-ATS‡	52.5	52.4	52.1
	Et-LI1a	8.1	7.8	7.4
	Et-LI1	−1.8	−2.4	−3.3
2	Et-LI1	0.0	0.0	0.0
	Et-LI2-ATS‡	52.3	52.6	53.1
	Et-LI2a	3.9	4.1	4.5
	Et-LI2	−0.1	−0.4	−1.1
3	Et-LI1	0.0	0.0	0.0
	Et-ZMTP-ATS‡	55.2	55.0	54.7
	Et-ZMTPa	9.9	8.5	8.1
	Et-LI1 + Et_2S	19.4	4.1	−7.4
	^{i}Pr			
1	^{i}Pr-ZDDP	0.0	0.0	0.0
	^{i}Pr-LI1-ATS‡	45.5	44.9	44.3
	^{i}Pr-LI1a	8.7	8.3	7.9
	^{i}Pr-LI1	−0.2	−0.8	−1.8
2	^{i}Pr-LI1	0.0	0.0	0.0
	^{i}Pr-LI2-ATS‡	46.6	46.6	46.9
	^{i}Pr-LI2a	8.5	8.7	9.3
	^{i}Pr-LI2	2.9	3.3	4.1
3	^{i}Pr-LI1	0.0	0.0	0.0
	^{i}Pr-ZMTP-ATS‡	48.9	48.5	48.1
	^{i}Pr-ZMTPa	13.4	12.5	11.4
	^{i}Pr-LI2 + $^{i}Pr_2S$	22.2	5.9	−6.1
	^{i}Bu			
1	^{i}Bu-ZDDP	0.0	0.0	0.0
	^{i}Bu-LI1-ATS‡	50.1	51.6	53.0
	^{i}Bu-LI1a	7.7	8.7	9.2
	^{i}Bu-LI1	−1.1	−0.2	−0.2
2	^{i}Bu-LI1	0.0	0.0	0.0
	^{i}Bu-LI2-ATS‡	51.0	51.8	53.2
	^{i}Bu-LI2a	3.3	3.9	5.2
	^{i}Bu-LI2	−0.7	0.3	2.1
3	^{i}Bu-LI1	0.0	0.0	0.0
	^{i}Bu-ZMTP-ATS‡	53.3	53.6	54.6
	^{i}Bu-ZMTPa	7.2	7.8	9.1
	^{i}Bu-ZMTP + $^{i}Bu_2S$	19.2	2.6	−9.2

[a] All energies are in kcal/mol and include ZPVE corrections. [b] The numbers identifying the reactions correspond to those given in Scheme 2. [c] The species are identified according to the nomenclature explained in the text. [d] The values in parentheses indicate the temperature in kelvin.

between the mechanisms of alkyl group transfer and hydrogen transfer is only present in the transition state.

The energetic data for reaction **1** show that the barrier to isomerization is smallest for the H-substituted system while the energetic barriers for the alkyl-substituted ZDDPs are at least 12 kcal/mol higher. The barrier for the H-substituted system is smaller because substantial bonding exists between the hydrogen atom and the rest of the ZDDP molecule throughout the course of the reaction which prevents the accumulation of charge on the hydrogen atom that is being transferred. On the other hand, the data for the alkyl-substituted species showed that the alkyl group was transferred with a slightly positive charge due to a decrease in the total bonding between this group and the remainder of the ZDDP molecule which decreases the stability of the transition state. The positive charge formed in the transition states for the alkyl-substituted species would formally be located on the α-carbon of the alkyl group following heterolytic cleavage of the C−O bond in the transition state. In the ^{i}Pr-substituted system the positive charge is stabilized due to slight electron donation effects from the two substituents on the α-carbon which decreases the energetic barrier to the reaction. When C−O bond dissociation occurs for the other alkyl substituents considered in this study, Et and ^{i}Bu, primary carbocations with minimal stabilization are formed, and accordingly the energetic barriers are larger. In all cases the value of the barrier exhibits only minimal temperature dependence, and as expected the products are more stable than the intermediates.

The larger barrier for the alkyl-substituted systems is a result of the heterolytic cleavage of the C−O bond which results in the separation of charge across the bond. It may be thought that homolytic cleavage of the C−O bond to result in the transfer of the alkyl group as a radical would be energetically preferred since the significant separation of charge would be avoided. In fact, previous simulations have shown that ZDDP molecules can decompose through the elimination of alkyl radicals,[28] and hence the formation of a radical through homolytic cleavage of the C−O bond is not unreasonable. Despite several attempts to locate such a mechanism no process consistent with an alkyl radical transfer was found. Instead, the only intramolecular alkyl group transfer process that was observed was that discussed above involving transfer of the alkyl group as a slightly positive species. The same holds true for the mechanisms of reactions 2 and 3 which are discussed below.

The mechanism described above for reaction 1 leads to the formation of the R-LI1 linkage isomer. As noted previously further alkyl group transfer within this molecule can occur according to either of reactions 2 and 3. Structural and energetic data for these reactions are given in Figure 4 and Table 2, respectively. The calculations showed that the details of the geometric and electronic structures of the stationary points located along the reaction pathway for reaction 2 were analogous to those discussed above for reaction 1. Furthermore, the energetic barriers and trends for reaction 2 were quite similar to those observed for reaction 1 and can be interpreted similarly. This is not surprising since these two reactions occur through virtually identical processes and should only be minimally affected by the difference between the reactant R-ZDDP molecule in reaction 1 and the reactant R-LI1 molecule in reaction 2. Because of the similarity in the geometric and energetic details of the mechanisms for these reactions, the latter will not be discussed in detail.

Reaction 3 involves the transfer of an alkyl group from an oxygen atom to the alkylated sulfur in R-LI1 to form R-ZMTP through the elimination of a dialkyl sulfide. For the H-substituted species reaction 3 occurs through a process similar to that described above for reactions 1 and 2. The main difference is that in reaction 3 the Zn−S bond does not undergo any appreciable change as the system moves toward the transition state while the P−S bond distance increases by a significant amount. The bond order and charge data (see Table 1S in the Supporting Information) indicate that this process is consistent with a concerted hydrogen atom transfer analogous to that described above for reaction 1. In the transition state the P−S bond length has increased to 2.442 Å, which is significantly longer than the original value of 2.111 Å in the H-LI1 reactant. The P−S bond order has also decreased to a value of 0.50 from an initial value of 0.96, which indicates that this bond has undergone significant dissociation, but interaction between these two atoms still exists in the transition state. In the H-ZMTPa adduct the P−S bond distance has increased to 2.811 Å, and the electronic energy is more stable than that of the dissociated product due to favorable electronic interactions between H_2S and the remainder of the adduct. The free energy values indicate that dissociation of the adduct to form the separated products is favored at higher temperature.

For alkyl-substituted ZDDPs the mechanism of reaction 3 was found to be different than that of the H-substituted system and involved the transfer of the alkyl group as a species with a slightly positive charge. This process is similar to that discussed above for reactions 1 and 2. It is interesting to note that for reaction 3 the P−S bond distance in the transition states of the alkyl-substituted species is approximately 0.2 Å shorter than the analogous distance in H-ZMTP-ATS‡. The P−S bond orders in the alkyl-substituted transition states are all approximately 0.75, which indicates that bonding between the R_2S group and the phosphorus atom of ZMTP is present to a greater degree in all of the alkyl-substituted transition states than in the H-substituted case. The shorter P−S bond length is due to the fact that the S−R bond, and hence the dialkyl sulfide, is not nearly as completely formed in the R-ZMTP-ATS‡ transition states, where R is a non-hydrogen substituent, as it is in H-ZMTP-ATS‡. The increased interaction between the dialkyl sulfide and the R-ZMTP molecule is apparent in the electronic energies which indicate that the R-ZMTPa adduct is substantially more stable than the dissociated products. As expected, when temperature effects are considered, the free energy values favor dissociation of the adduct to yield the product.

Thus, it is apparent that alkyl group transfer to yield a dialkyl sulfide and R-ZMTP occurs through a mechanism similar to the alkyl group transfer mechanisms that were located for reactions 1 and 2. The electronic and free energy barriers for reaction 3 all exhibit the same trends that were discussed above for the previous two reactions and are due to the relative abilities of the alkyl groups to stabilize the positive charge formed at the α-carbon during the alkyl group transfer. In all cases the barrier for reaction 3 was a few kcal/mol higher than that of reactions 1 and 2 for the system with the same substituents. The increased barrier for reaction 3 is most likely due to the fact that the dissociation of the P−S bond in this reaction incurs a larger energetic penalty than the partial dissociation of the Zn−S bond in reactions 1 and 2. The larger barrier for reaction 3 may be significant since, as noted above, R-LI1 can undergo alkyl group transfer to yield either R-LI2 or R-ZMTP, and the latter process may be kinetically disfavored. The effect of the energetic details of these reactions on the overall formation of antiwear films is explored in greater detail in part d of the discussion.

c. Mechanism of Olefin Elimination. The formation of olefins during the decomposition of ZDDP additives is observed experimentally.[23,24] It has been suggested that this reaction occurs through either of the mechanisms denoted “b” or “c” in Scheme 1, both of which involve the transfer of a β-hydrogen atom from one of the alkyl groups to an adjacent sulfur atom.[23,24] Recently, a theoretical study of the finite temperature behavior of ZDDPs has also provided evidence in favor of olefin elimination through β-hydrogen transfer.[28] In this part of the discussion the olefin elimination mechanism will be explored for the Et-, ^{i}Pr-, and ^{i}Bu-substituted species. The H-substituted ZDDP molecule cannot participate in this reaction due to the lack of alkyl groups and will not be considered.

Attempts were made to locate mechanisms consistent with both of those labeled “b” and “c” in Scheme 1; however, only one pathway was identified. The mechanism of olefin elimination was found to be similar for all types of substituents that were considered and will be examined in a general sense with information regarding specific substituents given as appropriate. The naming scheme that will be used to identify the reactants, products, transition states, and intermediates is similar to that used in sections IIIa and IIIb. The reactants and products will be identified by the same names that were introduced in part a. The transition states will be labeled with a three-part name, where the first part indicates the type of substituent on the parent ZDDP molecule, the second part identifies the product formed from the transition state, and the third part is the label OETS‡ which indicates that this is an olefin elimination transition state. Thus, the transition states for reactions 4, 5, and 6 are labeled as R-LI1H-OETS‡, R-LI2H-OETS‡, and R-ZMTP-OETS‡, respectively, where R is the appropriate substituent label. Once again, intermediate structures corresponding to the direct products following the transition states were located. For reactions 4 and 5 these intermediates will be denoted with the letter “a” following the name of the product, and for reaction 6 the intermediate will be denoted with the label “Ha” after the name of the product to avoid confusion with the name of the intermediate for the alkyl group transfer discussed above. Thus, the intermediate structures will be labeled as R-LI1Ha, R-LI2Ha, and R-ZMTPHa for reactions 4, 5, and 6, respectively. The transition states connecting these intermediates to the final products were not located for the same reasons that were outlined above for the isomerization reactions. Energetic details of reactions 4−6 are given in Table 3, and structural data of the stationary points along the reaction pathways for each reaction are presented in Figure 5. Specific details of the electronic structure are given in the main text where appropriate, and a full set of such details is provided in Table 2S of the Supporting Information.

In reaction 4 the system is initially in the R-ZDDP form, and olefin elimination occurs through the transfer of a β-hydrogen from an alkyl group to one of the sulfur atoms. This process is facilitated by a decrease in the S−H distance due to the rotation of one of the alkyl groups from its position in the reactant ZDDP, which is apparent for all substituents from the structural data provided in Figure 5 as the system proceeds from the reactant to the transition state. In the transition state the S−H bond order has increased to ∼0.3 while the $C^β$−H bond order has decreased to ∼0.5 at this point during the reaction. An increase in the $C^α$−$C^β$ bond order was also observed to occur throughout the β-hydrogen transfer with the $C^α$−$C^β$ bond orders exhibiting values of ∼1.5 in the transition state for all types of substituents. In the transition states the $C^α$−O bond orders were all less than 0.20, which indicates that significant dissociation of this bond has taken place at this point during the reaction. An examination of the charges at the α-carbon in the transition states showed only small increases of $+0.014e$, $+0.043e$, and $+0.032e$ for the Et-, ^{i}Pr-, and ^{i}Bu-substituted species, respectively, when compared to the appropriate R-ZDDP molecule, which indicates that a carbonium ion is not formed during the olefin elimination reaction. This is most likely due to the increase in the $C^α$−$C^β$ double bond character which prevents the accumulation of positive charge at $C^α$. Including the charges

TABLE 3: Relative Electronic and Free Energies[a] for the Stationary Points along the Olefin Elimination Pathways for the Et-, ^{i}Pr-, and ^{i}Bu-Substituted ZDDPs Participating in Reactions 4−6

reaction[b]	species[c]	ΔE	$\Delta G(300)$[d]	$\Delta G(500)$[d]
	Et			
4	Et-ZDDP	0.0	0.0	0.0
	Et-LI1H-OETS‡	42.0	41.7	41.1
	Et-LI1Ha + C_2H_4	29.0	16.6	6.8
	Et-LI1H + C_2H_4	16.9	4.4	−5.5
5	Et-LI1H	0.0	0.0	0.0
	Et-LI2H-OETS‡	41.5	41.1	39.9
	Et-LI2Ha + C_2H_4	25.1	12.6	2.2
	Et-LI2H + C_2H_4	17.1	4.7	−5.5
6	Et-LI1H	0.0	0.0	0.0
	Et-ZMTP-OETS‡	47.1	46.6	45.4
	Et-ZMTPHa + C_2H_4	46.8	34.5	24.6
	Et-ZMTP + C_2H_4 + H_2S	34.3	10.7	−7.8
	^{i}Pr			
4	^{i}Pr-ZDDP	0.0	0.0	0.0
	^{i}Pr-LI1H-OETS‡	36.4	36.1	35.9
	^{i}Pr-LI1Ha + C_3H_6	28.1	13.5	2.5
	^{i}Pr-LI1H + C_3H_6	15.7	0.6	−11.2
5	^{i}Pr-LI1H	0.0	0.0	0.0
	^{i}Pr-LI2H−OETS‡	36.7	36.6	36.5
	^{i}Pr-LI2Ha + C_3H_6	25.1	10.9	0.1
	^{i}Pr-LI2H + C_3H_6	17.0	3.1	−7.6
6	^{i}Pr-LI1H	0.0	0.0	0.0
	^{i}Pr-ZMTP-OETS‡	42.2	42	41.7
	^{i}Pr-ZMTPHa + C_3H_6	46.7	32.8	22.5
	^{i}Pr-ZMTP + C_3H_6 + H_2S	34.3	9.1	−9.2
	^{i}Bu			
4	^{i}Bu-ZDDP	0.0	0.0	0.0
	^{i}Bu-LI1H-OETS‡	40.1	41.0	41.0
	^{i}Bu-LI1Ha + i-C_4H_8	22.7	9.0	−1.6
	^{i}Bu-LI1H + i-C_4H_8	10.3	−4.1	−15.5
5	^{i}Bu-LI1H	0.0	0.0	0.0
	^{i}Bu-LI2H-OETS‡	40.5	40.2	39.5
	^{i}Bu-LI2Ha + i-C_4H_8	18.5	3.3	−8.6
	^{i}Bu-LI2H + i-C_4H_8	10.4	−4.5	−16.3
6	^{i}Bu-LI1H	0.0	0.0	0.0
	^{i}Bu-ZMTP-OETS‡	44.8	44.6	44.0
	^{i}Bu-ZMTPHa + i-C_4H_8	40.1	25.2	13.8
	^{i}Bu-ZMTP + i-C_4H_8 + H_2S	27.7	1.5	−18.6

[a] All energies are in kcal/mol and include ZPVE corrections. [b] The numbers identifying the reactions correspond to those given in Scheme 2. [c] The species are identified according to the nomenclature explained in the text. [d] The values in parentheses indicate the temperature in kelvin.

on the groups bonded to the α-carbon in the charge calculation did not change this interpretation.

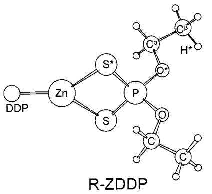
These results indicate that reaction 4 occurs through a concerted mechanism consistent with that labeled “b” in Scheme 1; however, in the transition state the C−O bond dissociation is completed to a greater degree than the other bond dissociation and formation processes involved in the reaction. The fact that this reaction was observed to occur through a concerted process is consistent with experimental evidence that shows that rearrangement of the alkyl group to a more stable carbocation does not occur during olefin elimination in the absence of acid.[23] It is noted that rearranged alkenes have been observed during the decomposition of ZDDPs in an acidic environment which indicates that other chemical species in the oil may influence the decomposition mechanism.[24] It is important to note that the phosphorus-containing product of acid-catalyzed olefin elimination would not differ from that here; however, the rate of elimination would likely be increased.

It was found that the geometric and electronic structure data of the atoms involved in the reactions leading to R-LI1Ha and R-LI1H were similar to those of the H-LI1a and H-LI1 molecules formed through alkyl group transfer. This is not surprising since the only difference between the alkyl and H-substituted species is the presence of an alkyl group on an oxygen atom not involved in the reaction. As a result of this similarity, the bonding and structures within these species can be interpreted in an analogous fashion to that described above for the H-substituted systems, and aside from saying that the intermediate and product are consistent with mechanism “b” in Scheme 1, these species will not be discussed further.

The energetics show that in all cases the barrier to reaction 4 is smaller than that of the intramolecular alkyl group transfer labeled reaction 1 that was discussed in part b. This is significant since both reactions start from the R-ZDDP molecule, and hence it appears that olefin elimination is kinetically favored over isomerization, at least from an energetic point of view. It was also found that the barrier for olefin elimination in reaction 4 is rather insensitive to temperature effects; however, a slight dependence upon the nature of the substituent was observed. The electronic and free energy barriers are smallest for the ^{i}Pr-substituted system at ∼36 kcal/mol, which is in relatively good agreement with the experimentally estimated value of 31 kcal/mol for the elimination of propene from isopropyl-substituted ZDDP.[23] The barrier for the ^{i}Bu-substituted system is the next largest (∼40 kcal/mol), and that for the elimination of ethene from Et-ZDDP is largest (∼42 kcal/mol). It may be thought that the observed substituent dependence is due to charge stabilization effects at the α-carbon as was observed in the case of alkyl group transfer. Such an interpretation would be correct if a process involving the formation of a carbonium ion took place; however, in the located transition state no appreciable accumulation of positive charge at the α-carbon was observed, and hence the observed substituent dependence must be of a different origin. It is known that the C−O bond energy is ∼3 kcal/mol less for secondary carbons than it is for primary ones.[55] In the transition state for the olefin elimination mechanism the C^{α}−O bond has undergone significant dissociation. The ^{i}Pr-substituted system may have a lower barrier since the dissociation of the C−O bond presents less of an energetic penalty for this system than that incurred in the case of either of the two other substituents. In all cases the final products of the reaction are more stable than the intermediate species, and the stabilities of both the intermediate and products with respect to the transition state increase with the temperature. This is expected due to the dissociation of the molecule through the elimination of the alkene which increases the entropy of these systems relative to that of the transition state where the olefin elimination has not been completed.

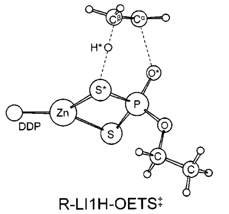
It was found that the mechanistic details of reaction 5, such as the geometries and energetic barrier, were similar to those discussed for reaction 4 for all substituents that were considered. Furthermore, the observed dependence of the magnitude of the barrier upon the type of substituent was similar to that observed for reaction 4 and likely arises from the same origin. The similarities between the mechanistic details of these two reactions are not surprising since the only difference between them is in the structure of the reactant, and this difference is only for atoms not actually involved in the reaction. As a result, the mechanism for reaction 5 will not be discussed in detail.

For all of the substituents that were considered it was found that the barrier to reaction 6 was approximately 5 kcal/mol higher than that for reaction 5. The mechanism itself was quite similar to that of reactions 4 and 5 and could be described as taking place through an analogous concerted process involving β-hydrogen transfer. The main structural difference is that in



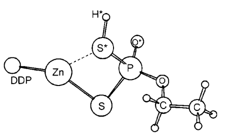
R-ZDDP

R	S*-H*	C$^{\beta}$-H*	C$^{\alpha}$-C$^{\beta}$	C$^{\alpha}$-O*
Et	5.540	1.094	1.517	1.454
^{i}Pr	4.714	1.095	1.522	1.471
^{i}Bu	5.500	1.101	1.528	1.455



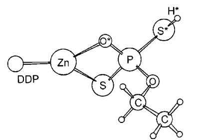
R-LI1H-OETS‡

R	S*-H*	C$^{\beta}$-H*	C$^{\alpha}$-C$^{\beta}$	C$^{\alpha}$-O*
Et	1.772	1.293	1.390	2.305
^{i}Pr	1.807	1.279	1.395	2.502
^{i}Bu	1.870	1.241	1.403	2.273



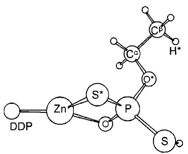
R-LI1Ha

R	S*-H*	Zn-O*	Zn-S*
Et	1.349	3.701	2.657
^{i}Pr	1.348	3.706	2.641
^{i}Bu	1.348	3.766	2.641



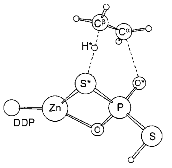
R-LI1H

R	S*-H*	Zn-O*	Zn-S*
Et	1.351	2.066	4.530
^{i}Pr	1.351	2.067	4.512
^{i}Bu	1.351	2.072	4.531



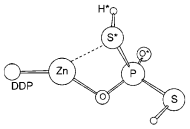
R-LI1H

R	S*-H*	C$^{\beta}$-H*	C$^{\alpha}$-C$^{\beta}$	C$^{\alpha}$-O*
Et	5.060	1.094	1.516	1.464
^{i}Pr	4.098	1.093	1.521	1.479
^{i}Bu	5.328	1.098	1.527	1.463



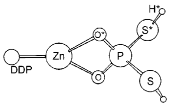
R-LI2H-OETS‡

R	S*-H*	C$^{\beta}$-H*	C$^{\alpha}$-C$^{\beta}$	C$^{\alpha}$-O*
Et	1.790	1.286	1.391	2.307
^{i}Pr	1.827	1.271	1.395	2.535
^{i}Bu	1.876	1.248	1.401	2.288



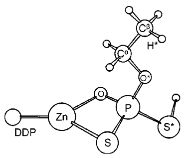
R-LI2Ha

R	S*-H*	Zn-O*	Zn-S*
Et	1.348	3.794	2.608
^{i}Pr	1.348	3.794	2.608
^{i}Bu	1.348	3.794	2.608



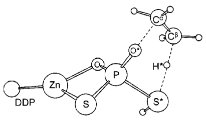
R-LI2H

R	S*-H*	Zn-O*	Zn-S*
Et	1.349	2.106	4.202
^{i}Pr	1.349	2.106	4.202
^{i}Bu	1.349	2.106	4.202



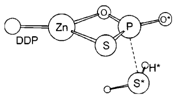
R-LI1H

R	S*-H*	C$^{\beta}$-H*	C$^{\alpha}$-C$^{\beta}$	C$^{\alpha}$-O*
Et	5.312	1.094	1.516	1.464
^{i}Pr	5.127	1.093	1.521	1.479
^{i}Bu	5.182	1.098	1.527	1.463



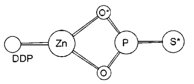
R-ZMTP-OETS‡

R	S*-H*	C$^{\beta}$-H*	C^{a}-C$^{\beta}$	C$^{\alpha}$-O*
Et	1.724	1.344	1.382	2.459
^{i}Pr	1.781	1.314	1.387	2.901
^{i}Bu	1.841	1.283	1.391	2.489



R-ZMTPHa

R	S*-H*	P-O*	P-S*
Et	1.348	1.479	2.811
^{i}Pr	1.348	1.479	2.811
^{i}Bu	1.348	1.479	2.811



R-ZMTP

R	Zn-O*	P-O*	P-S*
Et	2.112	1.538	1.906
^{i}Pr	2.112	1.538	1.906
^{i}Bu	2.112	1.538	1.906

Figure 5. Structures and relevant bond distances for the stationary points along the reaction pathways for reactions 4−6. Note that the structures shown all correspond to the Et-substituted species. The bond lengths given in the tables below each structure are in Å. Note that the unreacted DDP group has been replaced with the label DDP.

the transition state for reaction 6 the P−S bond is being broken instead of the Zn−S bond as in reactions 4 and 5. This difference is the likely origin of the larger barrier since the dissociation of the P−S bond in reaction 6 involves a larger energetic penalty than the dissociation of the Zn−S bond in either of reactions 4 and 5. For all of the substituents the elimination of the olefin leaves behind an adduct species, R-ZMTPHa, where a molecule of H_2S is coordinated to the phosphorus atom. In the final product the H_2S molecule has been removed from the system, and it is possible that this reaction is responsible for the evolution of this gas that is observed to take place during the experimental formation of ZDDP antiwear films.[21−23] The magnitude of the barrier for reaction 6 exhibited the same substituent dependencies as those observed for reactions 4 and 5. Once again, the substituent dependence exhibited by the barrier can be rationalized in terms of the strength of the C^{α}−O bond when different types of substituents are present on the molecule. The fact that the barrier to reaction 6 is larger than that to reaction 5 is interesting since it indicates that dissociation of R-LI1H to yield R-LI2H plus olefin is kinetically favored over the formation of R-ZMTP, olefin, and H_2S from an energetic point of view. The phosphorus-containing intermediates and products for all of the model alkyl-substituted systems are identical to the H-ZMTPa and H-ZMTP molecules discussed above and will not be elaborated upon here.

d. Interpretation of the Thermodynamic and Mechanistic Results within the Context of ZDDP Antiwear Film Formation. ZDDP antiwear films are thought to consist of an amorphous zinc poly(thio)phosphate network of the type shown in Figure 2.[15−20] The formation of this network is thought to occur through a polymerization process involving the formation of P−O−P and P−S−P linkages between (thio)phosphate subunits that are derived from ZDDP. The formation of these linkages requires the availability of low-coordinate phosphorus atoms that are receptive to nucleophiles and a supply of oxygen and sulfur atoms that can act as nucleophiles. The low-coordinate phosphorus atom in the decomposed DDP group of the R-ZMPT product of reactions 3 and 6 can readily undergo attack by various nucleophiles present in the oil, and hence this species satisfies the first criterion for linkage formation. In a previous theoretical study of the finite temperature behavior of R-ZDDP and R-LI1 it was shown that the coordination number at the zinc atom of these molecules fluctuates between two and four.[28] Presumably, this is also true for the products of the other reactions considered here which have similar bonding arrangements around the zinc atom. The change in coordination at the zinc atom occurs through the dissociation of Zn−O and Zn−S bonds which provide a source of oxygen and sulfur atoms, respectively, that can act as nucleophiles and react with the low-coordinate phosphorus atoms to form P−O−P and P−S−P linkages. Thus, it is apparent that R-ZDDP and the products of reactions 1−6 possess the attributes necessary to form antiwear films through the polymerization of (thio)phosphate subunits and hence may be important within the earlier stages of antiwear film formation. The fact that the sulfur- and carbon-containing products of these reactions are consistent with known byproducts of film formation is further evidence suggesting that these reactions take place during the formation of antiwear films.

Experimentally, it is observed that ZDDP antiwear films are not formed under ambient conditions but can be formed through the application of temperature and pressure. The general experimental procedure involved in the formation of antiwear films involves the addition of ZDDP additives to oil, which is initially at room temperature where film formation does not take place, followed by either heating to ~500 K or the application of pressure within wear testing devices to initiate the formation of the antiwear film. It is observed that film formation does not instantaneously take place at the higher temperature but occurs only after an induction period has been incurred. Since it is known that the antiwear films are not directly produced from ZDDP, but rather from species derived from this molecule, it has been proposed that the induction period is due to the accumulation of precursors to the antiwear film.[16] Reactions 1−6 explicitly involve the alkyl groups and lead to the formation of precursors to the antiwear films and hence an examination of the types of antiwear film precursors derived from these difference types of ZDDPs through these reactions may provide useful insight into experimentally observed aspects of the formation of antiwear films from different types of ZDDPs. In the following analysis the mechanistic and thermodynamic data presented above will be interpreted to determine the main reaction pathways that the different types of ZDDPs undergo to form precursors to the antiwear films. The identification of these pathways will provide insight into the origin of differences in the observed byproducts of film formation for different types of ZDDPs and also provide a basis for future investigations of how these precursors can react to form antiwear films.

The interpretation of the data will proceed in a fashion that mirrors the process employed to thermally produce antiwear films. First, the thermodynamic data at 300 K will be used to determine what form the system is in after it has spent enough time at this temperature to reach equilibrium. It is assumed that the temperature of the system is then increased from 300 to 500 K at a sufficiently fast rate such that the concentrations of the various chemical species cannot adjust to the changes in the relative free energies to establish a new equilibrium, and hence the initial concentrations of these species at 500 K will be similar to the equilibrium values at 300 K. The data at 500 K will then be applied to determine what reactions will take place at the higher temperature to yield precursors to the antiwear films. Overall, this analysis will allow for the identification of the series of reactions that lead to the formation of antiwear film precursors from the various types of ZDDP additives.

The H-ZDDP system can only participate in intramolecular hydrogen atom transfer, at least when exclusively considering reactions examined in this study, and hence the formation of H-ZMTP, which is imperative for film formation, can only take place through reaction 3. This reaction can only occur through the decomposition of H-LI1, and hence reaction 1 must precede reaction 3. The thermodynamic data at both temperatures show that H-ZDDP is energetically favored over either of the isomers which limits the likelihood that decomposition to H-ZMTP through reaction 3 will occurs since H-LI1 will not be available in significant quantities. The products of reaction 3 are energetically disfavored at both temperatures, which further decreases the probability that H-ZMTP will be formed. Overall, these results indicate that the system will persist in the H-ZDDP form which cannot directly react to form antiwear films, and it is unlikely that film formation will occur to an appreciable extent for the H-substituted system without the influence of other chemical species present in the oil that may initiate chemical decomposition of H-ZDDP. Experimentally, the H-ZDDP molecule is not used as an antiwear agent; hence, data do not exist to examine the validity of this conclusion, and these results will not be examined further.

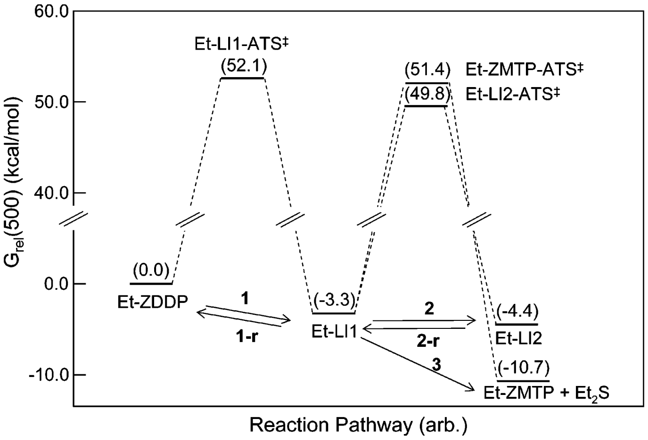


Figure 6. Reactions relevant to the formation of antiwear film precursors for the Et−ZDDP system. Relative free energies at 500 K of the stationary points for these reactions are given in parentheses. Note that the energetic barriers discussed in the text for a given reaction are the differences in the free energies of the transition state and reactant and do not correspond to the relative free energies of the transition states given in parentheses. Each reaction is identified according to the appropriate label above or below the appropriate arrow.

The calculated thermodynamic data for the Et-substituted system showed that the Et-LI1 and Et-LI2 isomeric forms are both energetically favored over the parent Et-ZDDP molecule at 300 K by 2.4 and 2.8 kcal/mol, respectively. Once equilibrium is reached at this temperature, the Et-LI1 and Et-LI2 isomers will be present in similar concentrations since they have similar free energies. These two molecules provide a source of sulfur and oxygen atoms that can react to form linkages between (thio)-phosphate subunits; however, no substantial supply of low-coordinate phosphorus atoms is available since the products of reactions 3 and 6 are both energetically disfavored at this temperature. This may be why film formation is not observed to occur at the lower temperature. When the temperature is increased to 500 K, the products of reactions 3−6 become energetically favored, and the decomposition reactions are likely to take place. Reaction 3 can occur directly through the decomposition of Et-LI1 that is already present in the oil, while reactions 5 and 6 require the availability of Et-LI1H which is derived from Et-ZDDP through reaction 4. Unfortunately, Et-ZDDP and Et-LI1H are not available to participate in olefin elimination reactions, or at best exist in very small quantities, since the system is initially in the Et-LI1 and Et-LI2 isomeric forms when the temperature is increased to 500 K. Et-ZDDP could be formed through the isomerization of Et-LI1; however, the thermodynamic and mechanistic details of the reactions that Et-LI1 and Et-LI2 take part in must be examined before the process of olefin elimination from Et-ZDDP can be considered. A series of reactions involving Et-ZDDP, Et-LI1, and Et-LI2 that are relevant to the formation of precursors to the antiwear film are given in Figure 6.

Et-LI2 can only undergo alkyl group transfer to yield Et-LI1 through the reverse of reaction 2, which is referred to as 2-r in Figure 6; however, the energetic details of this reaction are not favorable, and hence this reaction is not likely to occur. On the other hand, Et-LI1 can participate in three different alkyl group transfer reactions: reaction 2 which leads to the formation of Et-LI2; reaction 3 which leads to the irreversible decomposition of the molecule through the elimination of Et_2S; or the reverse of reaction 1, labeled 1-r in Figure 6, which will produce Et-

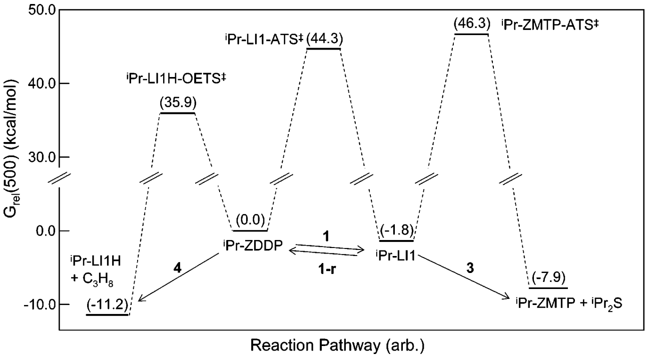


Figure 7. Reactions relevant to the formation of antiwear film precursors for the ^{i}Pr−ZDDP system. Relative free energies at 500 K of the stationary points for these reactions are given in parentheses. Note that the energetic barriers discussed in the text for a given reaction are the differences in the free energies of the transition state and reactant and do not correspond to the relative free energies of the transition states given in parentheses. Each reaction is identified according to the appropriate label above or below the appropriate arrow.

ZDDP. These three reactions all occur through the transfer of the same alkyl group through one of three similar mechanisms, and hence the relative rates of these reactions will primarily be determined by the energetic barriers of these reactions. The barrier to reaction 1-r is 55.4 kcal/mol, that to reaction 2 is 53.1 kcal/mol, and that to reaction 3 is 54.7 kcal/mol, and hence the isomerization of Et-LI1 to Et-LI2 will occur fastest, the elimination of Et$_2$S will be slightly slower, and the formation of Et-ZDDP will be slightly slower yet. When the fact that reaction 2 is kinetically favored is taken in combination with the thermodynamic data that indicate that the stability of Et-LI2 relative to Et-LI1 has increased with temperature, it is clear that Et-LI2 will always be present in the system. This is important because this molecule is a source of oxygen atoms that can react with the low-coordinate phosphorus atom of Et-ZMTP during the polymerization process. The formation of Et-ZMTP can occur through either the elimination of dialkyl sulfides from Et-LI1 or a series of olefin elimination reactions that are initiated by the formation of Et-ZDDP through reaction 1-r. It was mentioned above that reaction 3 should occur at a faster rate than 1-r, and hence the majority of the Et-LI1 remaining in the system after reaction 2 takes place will decompose through dialkyl sulfide elimination. The formation of Et-ZMTP through the elimination of Et$_2$S provides an explanation for the experimental observation that large quantities of dialkyl sulfides are produced during the formation of antiwear films from straight-chained primary alkyl ZDDPs.[21,22]

It should be noted that in this analysis it was assumed that the energetic barriers for these reactions are accurate; however, it is likely that errors of approximately 2−4 kcal/mol are associated with these values. If these errors are taken into account, it is more appropriate to suggest that reactions 1-r and 3 proceed at similar rates which will increase the amount of Et-ZDDP that eventually decomposes through olefin elimination. Nonetheless, the conclusion that the system will primarily participate in alkyl group transfer reactions to yield precursors to antiwear films still holds due to the fact that reaction 2 is overwhelmingly favored and since reaction 3 will still occur, albeit to a lesser extent.

The thermodynamic data for the ^{i}Pr-substituted system suggest that significant quantities of both ^{i}Pr-ZDDP and ^{i}Pr-LI1 should be present at 300 K, with the latter being favored by 0.8 kcal/mol. These molecules cannot react to form antiwear films in the absence of low-coordinate phosphorus atoms, and hence film formation will not occur at this temperature, which is consistent with experimental observations. The initial concentrations of ^{i}Pr-ZDDP and ^{i}Pr-LI1 at 500 K will be similar to the equilibrium values at 300 K, assuming that the temperature of the system is increased at a sufficiently fast rate. The thermodynamic data show that the stability of ^{i}Pr-LI1 increases by 1.8 kcal/mol relative to ^{i}Pr-ZDDP when the temperature is raised to 500 K, and at this temperature the products of the decomposition reactions (labeled 3−6) are all energetically favored (see Table 1). The ^{i}Pr-ZDDP molecule can directly take part in olefin elimination through reaction 4 or can isomerize through reaction 1. ^{i}Pr-LI1 can decompose through reaction 3, revert to ^{i}Pr-ZDDP through the reverse of reaction 1, labeled 1-r, or isomerize to ^{i}Pr-LI2 through reaction 2. The thermodynamics do not favor the last of these reactions, and it will not be examined in the following analysis. A series of reactions involving ^{i}Pr-ZDDP and ^{i}Pr-LI1 that are relevant to the formation of precursors to the antiwear films are given in Figure 7.

As mentioned above, ^{i}Pr-ZDDP can undergo either of reactions 1 or 4. The latter of these reactions is irreversible, since it leads to the decomposition of the molecule, and hence the kinetic data are most appropriate for its study. On the other hand, reaction 1 is reversible and will lead to an equilibrium between ^{i}Pr-ZDDP and ^{i}Pr-LI1 if ^{i}Pr-ZDDP remains in the oil long enough for this equilibrium to be established. It is necessary to determine the relative rates of reactions 1 and 4 in order to determine whether the ^{i}Pr-ZDDP molecule will persist in the system or be removed from the system through olefin elimination. The mechanistic data indicate that reaction 4 will occur at a significantly higher rate than reaction 1 for two reasons. First of all, the barrier to olefin elimination was calculated to be 8.4 kcal/mol lower than that to isomerization, and secondly in the reactive DDP group of ^{i}Pr-ZDDP 12 β-hydrogens are available to take part in olefin elimination vs two alkyl groups for isomerization, which further promotes olefin elimination over isomerization. Thus, it is clear that reaction 4 occurs at a significantly higher rate than reaction 1, which in turn implies that any ^{i}Pr-ZDDP present in the oil, either initially or formed through reaction 1-r at higher temperature, will rapidly decompose through olefin elimination on the time scales of these reactions; however, it remains to be seen if the formation of ^{i}Pr-ZDDP through reaction 1-r is likely to occur at higher temperature. It was mentioned above that ^{i}Pr-LI1 can either decompose through reaction 3 or isomerize through reaction 1-r. Once again kinetic factors will determine the relative probabilities of the occurrence of these reactions since reaction 3 is irreversible. In the case of alkyl group transfer within ^{i}Pr-LI1 the energetic barrier will have the most significant effect on the relative rates of these reactions since both processes start from the same type of molecule and involve the transfer of one specific alkyl group through two very similar mechanisms. The energetic barrier for reaction 3 is 48.1 kcal/mol while the barrier to 1-r was calculated to be 46.1 kcal/mol. Using the calculated values for the barriers it can be estimated that the rate of reaction 1-r will be ∼7.5 times greater than that of reaction 3. As a result, the majority of the ^{i}Pr-LI1 molecules initially present in the oil after heating will isomerize to form ^{i}Pr-ZDDP which, in turn, will rapidly decompose through olefin elimination as discussed above. Thus, the decomposition of ^{i}Pr-ZDDP through olefin elimination is the primary mode of precursor formation for the ^{i}Pr-substituted system. The ^{i}Pr-LI1H molecule cannot directly form antiwear films due to the absence of low-coordinate phosphorus atoms, and this molecule must undergo further reactions before film formation can take place. The energetic data at 500 K indicate that reactions 5 and 6 are likely to take place, and the products of these reactions, ^{i}Pr-LI2H and ^{i}Pr-ZMTP, provide a source of oxygen atoms and low-coordinate phosphorus atoms, respectively, that can participate in the formation of antiwear films. The formation of ^{i}Pr-ZMTP through reaction 6 occurs along with the elimination of H_2S and is likely the reason that the evolution of large quantities of this gas is observed during the formation of antiwear films from secondary alkyl ZDDPs.[21,22]

It is noted that the difference between the energetic barriers of reactions 1-r and 3 are within the intrinsic errors associated with these calculations. In the case that reaction 3 is slightly faster than reaction 1-r, the amount of ^{i}Pr-LI1 that decomposes through dialkyl sulfide elimination will be increased. However, it is noted that the ^{i}Pr-ZDDP present in the solution, either after the temperature is increased to 500 K or formed through reaction 1-r, will preferentially decompose through olefin elimination reactions. Thus, even when errors in the calculated energetic barriers are considered, it is clear that the ^{i}Pr-substituted system will still participate in olefin elimination reactions to a greater degree than the ethyl-substituted system.

An examination of the thermodynamic data at 300 K indicates that the ^{i}Bu-substituted system should demonstrate markedly different behavior than that observed for either of the Et- or ^{i}Pr-substituted systems. In particular, the data indicate that ^{i}Bu-ZDDP should decompose through olefin elimination at this temperature and that isomerization reactions should not occur to a significant extent. The free energies at 300 K indicate that ^{i}Bu-ZDDP should primarily decompose through olefin elimination as in reaction 4 to form ^{i}Bu-LI1H. This molecule can undergo further olefin elimination through either of reactions 5 or 6 to form ^{i}Bu-LI2H and ^{i}Bu-ZMTP, respectively. The thermodynamic data at 300 K (Table 1) show that the products of reaction 5 are more stable than those of reaction 4 from which they are formed while the products of reaction 6 are less favored. Since these reactions are irreversible, the kinetic details are more relevant to probability that they will occur and the energetic data (see Table 3) show that the barrier to reaction 5 is 4.3 kcal/mol lower than that to reaction 6. Overall, these data indicate that reaction 5 is significantly favored over reaction 6, assuming that the barriers are accurate, and hence ^{i}Bu-ZDDP will decompose through olefin elimination reactions at 300 K to form ^{i}Bu-LI2H. This molecule cannot directly form P−O−P linkages due to a lack of low-coordinate phosphorus atoms and is possibly the reason that film formation is not observed to take place under ambient conditions for branched primary alkyl ZDDPs. It is observed, however, that ZDDP antiwear films are formed from these additives at higher temperatures, and this process requires a supply of low-coordinate phosphorus atoms which can be produced through the either of reactions 3 or 6. The former requires the availability of ^{i}Bu-LI1 while the latter occurs through the decomposition of ^{i}Bu-LI1H. Unfortunately, the system has irreversibly decomposed to ^{i}Bu-LI2H at 300 K, and neither ^{i}Bu-LI nor ^{i}Bu-LI1H will be available to decompose at 500 K. Thus, in order for film formation to take place, ^{i}Bu-LI2H must decompose through reaction(s) other than those considered in this study. One such reaction involves the transfer of a hydrogen atom between the two hydrogenated sulfur atoms of ^{i}Bu-LI2H to release H_2S and form ^{i}Bu-ZMTP. The thermodynamic data indicate that the products of this reaction are favored by 2.4 kcal/mol over ^{i}Bu-LI2H at 500 K, and the barrier at this temperature was found to be 31.7 kcal/mol. These results indicated that this decomposition reaction is energetically favorable. The main byproduct of this reaction is H_2S gas, which is also observed to be produced during the experimental formation of antiwear films from ^{i}Bu-ZDDP, and hence this reaction is a possible decomposition route for this system; however, a more extensive study of the reactions that ^{i}Bu-LI2H can take part in is required before any definite conclusions can be made. The decomposition of ^{i}Bu-ZDDP through olefin elimination, and possibly H_2S elimination, is consistent with the experimental observation that the byproducts of the formation of antiwear films from branched primary alkyl ZDDPs are similar to those produced through the decomposition of secondary alkyl ZDDPs.[21,22]

Once again, it is noted that errors in the calculated energetics exist. If the energetics change such that reaction 6 becomes even more favored, the analysis is relatively unaltered. This is also true if the changes in the energetics favor reaction 5; however, in this case the formation of ZMTP would occur through this reaction which would preclude the need for further decomposition of LI2H to yield ZMTP. Overall, despite the possible changes in the energetics, it is clear that the ^{i}Bu-substituted system primarily decomposes through olefin elimination reactions.

IV. Conclusions

The mechanistic and thermodynamic details of the intramolecular alkyl group transfer and olefin reactions that ZDDP antiwear additives may take part in were examined with DFT methods. In particular, a set of reactions allowing for two consecutive olefin elimination or alkyl group transfers within a single DDP group was used. A series of substituents comprised of hydrogen, ethyl, isopropyl, and isobutyl groups was employed to investigate the dependence of the mechanistic and energetic details of these reactions upon the nature of the substituent. The differences in these details were used to elucidate the main reaction pathways that lead to the formation of precursors to antiwear films. The identification of these pathways provided insight into the origins of various byproducts of film formation and the observed differences in the rates of film formation for ZDDP additives with different types of alkyl substituents.

The energetic data showed that the H-substituted system should be relatively unreactive and remain in the H-ZDDP form. On the other hand, it was found that the alkyl-substituted systems should exist in different forms at finite temperature. In particular, it was found that Et-ZDDP should eventually decompose through intramolecular alkyl group transfer, while the decomposition of ^{i}Pr-ZDDP and ^{i}Bu-ZDDP is most likely to occur through olefin elimination. Differences between the H- and alkyl-substituted systems were also apparent through the mechanistic data which showed that for the H-substituted system hydrogen atom transfer occurs in a concerted fashion with the formation of the S−H bond and dissociation of the O−H bond occurring nearly simultaneously. For all of the alkyl-substituted systems the alkyl group transfer occurs through an asynchronous concerted mechanism where the C−O bond is significantly dissociated before the C−S bond has undergone substantial formation. It was also found that olefin elimination occurred through a concerted process involving the transfer of a β-hydrogen atom from one of the alkyl groups in the ZDDP molecule to an adjacent sulfur atom. This process is consistent with those proposed in previous studies.

The mechanistic and thermodynamic data were interpreted within the overall context of ZDDP antiwear film formation, and it was found that the results of this study could provide insight into experimentally observed aspects of the decomposition of ZDDPs. The most apparent observation is that H-ZDDP molecules should not readily form antiwear films and hence are not an appropriate model for the study of ZDDP antiwear film formation. This may be important in selecting model systems for future simulation studies of ZDDPs. It was found that all of the alkyl-substituted ZDDPs could react to produce precursors to antiwear films in different ways and that these differences can be related to observed aspects of antiwear film formation. The results showed that the Et-ZDDP system, a model for straight-chained primary alkyl ZDDPs, produced precursors to the antiwear films through alkyl group transfer reactions. The formation of Et-ZMTP through alkyl group transfer occurs through the elimination of Et_2S, and the fact that this reaction predominates for this system is consistent with the observation that large quantities of dialkyl sulfides are produced during the formation of films from straight-chained primary alkyl ZDDPs. The data for the ^{i}Pr-ZDDP system, a model for secondary alkyl ZDDPs, showed the molecule primarily decomposed through olefin elimination reactions and that ^{i}Pr-ZMTP should primarily be formed through the elimination of H_2S gas, which is also consistent with experiment. The ^{i}Bu-ZDDP system, a model for branched primary alkyl ZDDPs, was also found to undergo olefin elimination; however, the main decomposition pathway results in a product that cannot directly form antiwear films, and further decomposition to yield ^{i}Bu-ZMTP is necessary. A reaction that yields this product through the elimination of H_2S gas from ^{i}Bu-LI2H was briefly investigated and proposed as a possible decomposition route; however, further study is necessary before definite conclusions regarding the fate of ^{i}Bu-ZDDP can be made.

Thus, we have examined the reaction pathways leading to the formation of ZDDP antiwear film precursors for several different types of ZDDP additives. The identification of the precursors to film formation is a key step in the overall elucidation of a mechanism of antiwear film formation, and the details of this study will provide a basis for future theoretical studies of how the precursors can interaction with one another to yield structures consistent with antiwear films.

Acknowledgment. We gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada (NSERC), General Motors Canada, and General Motors Research and Development for financial support. Computing resources made available by the Canadian Foundation for Innovation, the Ontario Innovation Trust, SHARCnet of Canada, and the Academic Development Fund at the University of Western Ontario are also acknowledged.

Supporting Information Available: Cartesian coordinates and total energies of all optimized stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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