

ReaxFF investigations on effects of molecular substituents on lubricant additive decomposition: phosphate esters on ferrous surfaces

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Molecular dissociation is the first step in the formation of tribofilms from lubricant additives. We investigate the dissociation of phosphate ester additives on ferrous surfaces through reactive molecular dynamics (ReaxFF). By analysing the bond cleavage/formation, we identify the rate-limiting chemical mechanisms on several ferrous surfaces. Different molecular substituents are found to yield thermal stability in the following order: tertiary alkyl < secondary alkyl < primary linear alkyl \approx primary branched alkyl < aryl, in agreement with experimental observations. The effects of shear on mechanochemical decomposition are studied and compared to the purely thermal case.

Keywords: mechanochemistry, phosphate esters, additives, reaxff, substituents.

1. Introduction

Tribofilms play a crucial role in reducing friction and wear in lubricated systems. Understanding the mechanochemical reactions that drive the film formation of lubricant additives, such as the ubiquitous ZDDP, could guide the design of future additives. In our work, we employ ReaxFF to model the decomposition of phosphate esters with different substituents on ferrous surfaces, both purely thermal and under shear. The insights gathered underpin experimental results and are expected to have impacts in the molecular structure of other additives, namely ZDDP.

2. Methods

We employ the ReaxFF[1] reactive force field in Molecular Dynamics simulations of phosphate esters on different ferrous systems. These simulations can model scales inaccessible to ab initio methods and thus investigate complex mechanochemical reactions in realistic conditions. Our work includes thermal decomposition, representative of Vapor Phase Lubrication, and sliding-wall simulations representative of tribological systems. By analyzing the bond cleavage/stability of the different bonds in the additives, as well as the effects of temperature, pressure, and surface composition at the nanoscale, we investigate the molecular decomposition that would lead to subsequent tribofilm formation, as well as the behaviour of different molecular substituents.

2.1. Systems

For the phosphate ester additives, we study tertiary, secondary, primary linear and primary branched alkyls, and aryls.

α -Fe(110), Fe₃O₄(001) and hydroxylated, amorphous Fe₃O₄ substrates are employed for the substrates, which aim to represent the heterogeneous ferrous substrates observed experimentally.

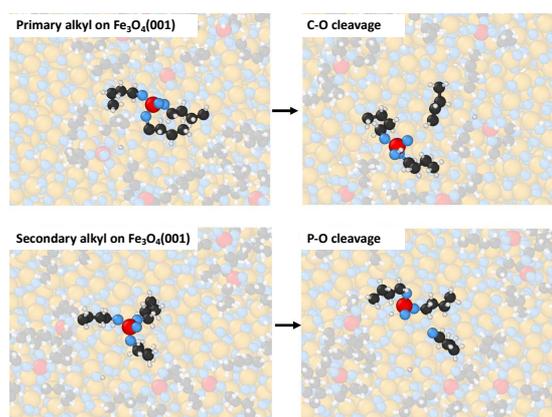


Figure 1 : Representative snapshots of phosphate ester molecules undergoing C-O (top, primary alkyl) and P-O (bottom, secondary alkyl) cleavage on a Fe₃O₄(001) [2]

3. Discussion

Decomposition rates were much higher on Fe₃O₄(001) and particularly α -Fe compared to hydroxylated, amorphous Fe₃O₄. This suggests that water passivates ferrous surfaces and inhibits phosphate ester chemisorption, decomposition, and ultimately film formation. On Fe₃O₄ decomposition proceeds mainly through C-O cleavage (to form surface alkyl and aryl groups) and C-H cleavage (to form surface hydroxyls). The onset temperature for C-O cleavage on Fe₃O₄ increases in the order: tertiary alkyl < secondary alkyl < primary linear alkyl \approx primary branched alkyl < aryl, in agreement with experimental observations for the thermal stability of antiwear additives with similar substituents.

4. References

- [1] Senftle, T.P. et al., "The ReaxFF reactive force-field: development, applications and future directions", *Npj Comput. Mater.* 2,1, 2016, 15011.
- [2] Ewen, J.P. et al., "Substituent Effects on the Thermal Decomposition of Phosphate Esters on Ferrous Surfaces", *J. Phys. Chem. C*, 124, 18, 2020, 9852–9865