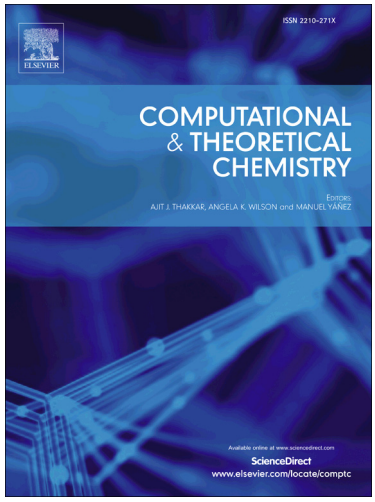

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ABSTRACT

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

Introduction

Zinc dialkyldithiophosphates (ZDDPs) has been used as an additive for a long time in the formulation of lubricating oils by petrochemical industries.[1,2] They were originally added to engine oils as antioxidants, as the same role of other antioxidants, such as cuprous dialkyldithiophosphate (CuDDP), organic molybdenum compounds (OMCs), and aromatic amines, *etc*.[3-6] However, it was also found that it can act as a dispersant, a corrosion inhibitor and a detergent, especially as an anti-wear agent.[7-9] Due to the two most attractive performances (anti-wear and anti-oxidant functions) of ZDDP additives, they have been attracted much attention and have been widely investigated in the past decades. A good understanding of the substituent effect on the structure and property of ZDDP would be useful in the intelligent selection and design of alternative anti-wear additives. Although experimental studies are straightforward, they are often time-consuming, expensive, and wearisome. Alternatively, computational chemistry is a useful and powerful approach to obtain valuable information and predict some molecular parameters directly related to the