Center for Quantum Science and Engineering (CQSE)

Weekly Seminar
Jan. 7, 2011 (Friday)

TIME Jan. 7, 14:30 ~ 15:30
TITLE Computational Study of the Substitution Effect on the Mechanism for the Aza-, Phospha- and Arsa-Wittig Reactions
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Abstract

The aza-, phospha- and arsa-Wittig reactions HM=PH3 + O=CHX HM=CHX + O=PH3 (M = N, P, As; X = H, F, Cl, Me, OMe, NMe2, CMe3) were examined using the density functional theory calculations. All of the structures were completely optimized at the B3LYP/6-311++G** level of theory. The main finding of this work is that the configuration mixing model can successfully predict the relative ordering of the activation energy and reaction enthalpies of the aza-, phospha- and arsa-Wittig reactions. It was demonstrated that O=CHX with more electro-releasing substituents will possess a smaller singlet-triplet splitting. This will facilitate the aza-, phospha- and arsa-Wittig reactions and will result in a larger exothermicity. In addition, the difference between singlet-triplet splitting of O=CHX and HM=PH3 play an important role in determining the kinetic and thermodynamic stability of the aza-, phospha- and arsa-Wittig reactions. When HM=PH3 with more ylidic character is utilized, the reaction has a smaller activation energy and a larger exothermicity.