Natural Bond Orbital Analysis of the Wittig Reaction

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Introduction

Wittig olefination is a common reaction for converting aldehydes or ketones into alkenes. The reaction is facilitated by a phosphonium ylide, $Y_3P–CR_2$, where the Y substituents are usually phenyl groups (Ph) and R substituents are either H atoms or alkyl groups. For example, the reaction of methylenetriphenylphosphorane, $Ph_3P–CH_2$, with formaldehyde, $CH_2=O$,

yields triphenylphosphonium oxide, $Ph_3P–O$, and ethylene, $CH_2=CH_2$. The reaction is understood to occur in two steps, with the first step forming a cyclic oxaphosphetane intermediate which subsequently proceeds to eliminate the alkene.

In this study we use computational chemistry methods to explore the Wittig reaction of phosphonium ylide (Y=H, CH_3, Ph) with formaldehyde in aqueous solution. Analysis of these reactions allowed us to examine the redistribution of electron density—the making and breaking of chemical bonds—across both steps of the reaction.

Methods

Gaussian-16 calculations were performed at the B3LYP/cc-pVDZ level using an implicit solvent model (scrf=pcm,smd) to approximate the aqueous environment of the reaction. All geometries were optimized using "tight" convergence thresholds. Vibrational frequency calculations were performed to characterize the nature of each stationary geometry (equilibrium or transition state). Intrinsic reaction coordinate (IRC) calculations mapped the minimum energy surface from reactants to products. Natural bond orbital (NBO) and natural resonance theory (NRT) analysis was performed using the NBO7 program

Reaction Profiles

The following are the calculated reaction profiles for the conversion of formaldehyde, $CH_2=O$, to ethylene, $CH_2=CH_2$. Reactions on hydrogen-, methyl-, and phenyl-substituted phosphonium ylides are considered.

Intrinsic Reaction Coordinate Pathways

IRC calculations were performed to determine the minimum energy pathway from reactants to products for the methyl-substituted reaction. The following plot shows the IRC for the first reaction step. The transition state is at IRC=0.00.

A separate IRC calculation shows the second step of the reaction as the intermediate eliminates ethylene.

Natural Resonance Theory Analysis

The *natural bond orders* of NRT analysis reveal the making and breaking of bonds across the IRCs. The following plots show the variation in bond orders for the first and second reaction steps.

Electronic Rearrangement

Plots of pNLMOs across the IRCs show how electron pairs undergo rearrangement during the reaction steps. The following show how a C lone pair transforms into a CC bond and a CO π bond becomes a PO bond during the first reaction step.

In the second step a CP bond becomes the CC π bond while a CO bond transforms into an O lone pair.

The orbital transformations shown above are consistent with the following curved-arrow representation of the mechanism for the Wittig reaction.

Donor-Acceptor Interactions

Orbital interactions facilitate bond rearrangement in the Wittig reaction. The following two interactions between the ylide and formaldehyde promote the formation of the oxaphosphetane intermediate.

On the left, a C lone pair donates about 0.19 electrons into an unfilled CO π antibond. This interaction gives rise to C-C bonding character while acting to cleave the CO bond. On the right, a CO π bond donates a small amount of electron density into an unfilled PC antibond. This yields some P-O bonding character while weakening the P-C interaction.

A single important donor-acceptor interaction is evident as the oxaphosphetane intermediate eliminates ethylene. This interaction, shown below, involves the donation of 0.04 electrons from the PC bond (on the left) into the CO antibond (on the right). This interaction is ultimately responsible for C-C π bonding character, that is the formation of the second CC bond of the $CH_2=CH_2$ product.

Conclusions

NBO/NRT analysis reveals bond breaking and making processes for the Wittig reaction that are consistent with the mechanism as understood by organic chemistry. These processes are facilitated by donor-acceptor interactions.

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