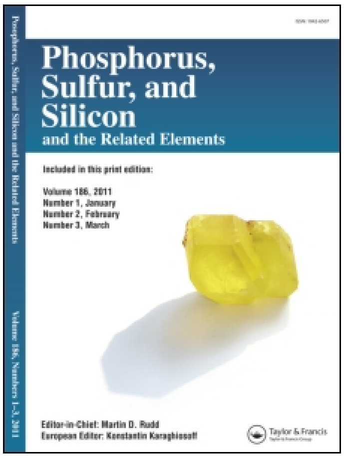

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The Interactions of Cyclophosphazenes with Olefin Containing Exocyclic Groups

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THE INTERACTIONS OF CYCLOPHOSPHAZENES WITH OLEFIN CONTAINING EXOCYCLIC GROUPS

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Density functional calculations on the series $N_3P_3F_5R$($R{=}CH_2CH_3$, $CH{=}CH_2$, $C{\equiv}CH$) show that the phosphazene substituent effect is similar to that of CF_3 and is dominated by σ bond polarity. UV-photoelectron measurements also favor a σ bond polarization effect. Calculations on $N_3P_3F_5ECH{=}CH_2$ ($E{=}O$, CH_2) and photoelectron spectroscopy of the vinyloxy derivative show the strong electronic effect of the phosphazene, which is dominated by the σ bond polarization mechanism. Extensive NMR correlations for substituted vinyloxy phosphazenes indicate the sensitivity of these effects to the nature of the ring substituents. The reactivity ratio and NMR data for styryloxy phosphazenes demonstrate the absence of significant mesomeric interactions.

Keywords: Cyclophosphazenes; DFT calculations; NMR; photoelectron spectroscopy

INTRODUCTION

One of the reoccurrent problems in main group chemistry is the nature of the electronic interaction between an unsaturated organic moiety and a second row atom, particularly those which are part of a structural unit exhibiting some degree of formal unsaturation. In cyclophosphazene chemistry, previous studies have focused on aryl derivatives in which the preponderance of the evidence favors a σ-polarization over a π-conjugation model.[1] The extension of this question to alkenyl- and alkynlphosphazenes is of interest from a fundamental perspective and as a basis for evaluation of cyclophosphazenes with olefin substituents for monomers in olefin addition polymerization reactions.[2]

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This investigation involves the combination of computational, spectroscopic, and kinetic methologies to provide an internally self-consistent model of the electronic effect of cyclophosphazenes on an unsaturated organic unit.

RESULTS AND DISCUSSION

We have carried out density functional calculations (33PW91/G31G*) on the series $N_3P_3F_5R$ ($R{=}C_2H_5$, $CH_2CH{=}CH_2$, $CH{=}CH_2$, $C{\equiv}CH$) and $N_3P_3F_5OR$($R{=}CH_2CH{=}CH_2$, $CH{=}CH_2$) and compared the results to model olefins. As opposed to strongly conjugating groups such as NO_2 and CN, the phosphazene and CF_3 groups reduce the electron population in a directly bonded vinyl group only by a small amount. Similar effects are noted in the carbon-carbon bond orders. The phosphorus-carbon bond orders are all less than one and show little variation between saturated and unsaturated substituents. A consideration of the NBO formal charges on phosphorus and nitrogen indicate that modulation of charges on phosphorus induced by substituents is compensated by electron transfer from the endocyclic nitrogen atoms.

Ongoing from free olefins to phosphazene bound olefins, an O.5eV stabilization of the organic π system is observed by ultraviolet photoelectron spectroscopy (UPS).[3] Direct conjugation of the organic and inorganic π systems would lead to destabilization. Consequently, either the π system is delocalized to phosphorus acceptor (d or σ^*) orbitals or sigma polarization leads to the stabilization. Olefins with electron-donating substituents do not show any increase in stabilization, thus favoring the σ-polarization model. Similar results have been obtained for alkynlphosphazenes.[3] Reactivity ratios of olefin phosphazenes indicate a polar, electronically isolated olefin.[4]

The near similarity in the calculated carbon-carbon bond order in $N_3P_3F_5OR$ ($R{=}CH_2CH{=}CH_2$, $CH{=}CH_2$) and the significant calculated ionic character of the phosphorus-oxygen bond argue for electronic isolation of the organic π system. The UPS data for the vinyloxyphosphazenes show ionization energies in the range associated with vinylacetate rather than vinylethers.[5] This observation is indicative of a system in which the olefin is highly polarized by σ-electron withdrawing effects but does not undergo significant conjugative interactions. The σ electronic effect, however, can be manifested across the phosphazene ring as shown by NMR correlations of the β-^{13}C and endocyclic ^{31}P chemical shifts.[5] Variations of substituents at a distant phosphorus site leads to observable changes in the vinyloxy ^{13}C chemical shifts. In copolymerization reactions, $N_3P_3Cl_5OCH{=}CH_2$ behaves like vinylacetate.

We have also examined the $N_3P_3X_5OC_6H_4CH{=}CH_2$ and $N_4P_4X_7OC_6H_4CH{=}CH_2$ (X=F, Cl) systems. The β olefin ^{13}C chemical shifts are essential invariant in this series. Given the sensitivity of the β ^{13}C data to π charge density in the olefin, this indicates that the olefin electronic structure is uneffected by the nature of the phosphazene substituent. The monomer reactivity ratios for $N_3P_3F_5OC_6H_4CH{=}CH_2$/p-$CH_3OC_6H_4CH{=}CH_2$ have been determined. The derived Alfrey-Price parameters for the $N_3P_3F_5O$ unit show that the resonance effect of the oxyphosphazene unit is negligible relative to styrene, but the polarity of the olefin is significantly different.

In summary, the data definitively show that the electronic effect of the phosphazene is based on sigma polarization rather than π conjugation. This effect, however, can be manifested across several atomic units within the phosphazene containing molecule.

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