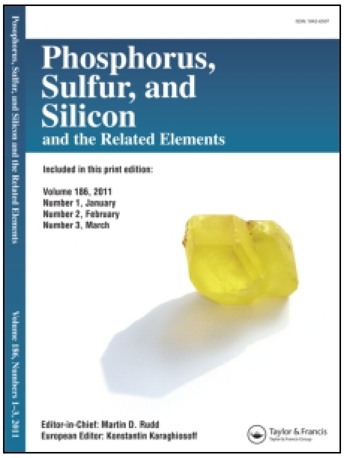

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Allen, Christopher W. , Calichman, Michael and Freund, Amy S.(2008) 'The Mechanism of the Reaction of Alkai Metal Phenoxides with Hexahalocyclotriphosphazenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 183: 2, 479 — 482

To link to this Article: DOI: 10.1080/10426500701761425

URL: http://dx.doi.org/10.1080/10426500701761425

Phosphorus, Sulfur, and Silicon, 183:479–482, 2008
Copyright © Taylor & Francis Group, LLC
ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500701761425

The Mechanism of the Reaction of Alkai Metal Phenoxides with Hexahalocyclotriphosphazenes

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*In both specific reaction rate studies and in intermolecular competition reactions, sodium phenoxide preferentially reacts with hexafluorocyclotriphosphazene (**1**) over hexachlorocyclotriphosphazene (**2**). In an intramolecular competition experiment using difluorotetrachlorocyclotriphosphazene (**3**), sodium phenoxide reacts exclusively at the fluorinated phosphorus site. These results are consistent with the NBO charges at the phosphorus centers. DFT calculations also indicate that in the case of pentacoordinate intermediate formation, an associative mechanism is kinetically favored. The variations of the rate of reaction of **2** with temperature, solvent and alkali metal cation have been determined. The activation parameters for the chlorophosphazene system show positive enthalpies and entropies of activation. The reaction rates of **2** increase with solvent basicity. The rates of reaction for the heavier alkali metal cations are greater than those for the lighter cations. The addition of a crown ether results in a significant rate increase. Consideration of all of these data suggest a mechanism where the rate has a major contribution from a preequilibrium wherein the metal phenoxide cluster dissociates into kinetically active speicies which adds, in the rate determining step, to the phosphorus (V) center.*

Keywords Cyclophosphazenes; kinetics; phosphazene reaction mechanisms; phenoxyphosphazenes

INTRODUCTION

Studies of the reactivity and mechanism of the nucleophilic substitution reactions of the cyclophosphazenes has proven to be a rich and fruitful area of research.[1–3] In depth investigations of the stereo- and regio pathways followed in the reactions of hexachlorocyclotriphosphazene and the origins of stereoselectivity and mechanisms of these reactions

Partial support from the National Science Foundation under the Vermont EPSCoR program (ESP0236976) is gratefully acknowledged.

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where primary and secondary amines serve as the nuclecophile have been reported. Significantly less attention has been given to reactions of oxyanions, studies of the fluorocyclotriphosphazenes[4] and to the dependence of the rates and mechanisms as a function of the identity of the halogen atom. A central dogma of the reactivity of halocyclophosphazenes is that the relative rates of reaction decrease through the series of bromide, chloride, fluoride.[2] This is based on the work of Moeller who reported the relative rates of the reactions of $N_3P_3X_6(X = Br, Cl, F)$ with n-propylamine.[5] Thus the presumption[2] has been that the rates are controlled by relative ease of phosphorus-halogen bond cleavage. On the other hand, computational studies employing both ab initio and DFT methods[6,7] clearly show that the natural bond order (NBO) changes on the phosphorus atoms are highest for the fluorophosphazenes, which suggest that the fluoro derivatives would be most susceptible to attack by a nucleophilic reagent. In this article, we provide a preliminary report of the relative rates of reaction of the phenoxide ion, a prototypical oxyanion in phosphazene chemistry, with hexafluorocyclotriphosphazene, $N_3P_3F_6$(**1**) and hexachlorocyclotriphosphazene, $N_3P_3Cl_6$(**2**) and detailed kinetic studies of the variables in the reactions of alkai metal phenoxyides with **2**.

EXPERIMENTAL

Kinetics measurements were obtained using ^{31}P NMR[4] for reactions of **2**. Due to the complexity of the NMR spectra of 1, GC-MS with selected ion monitoring was used to determine the kinetics of the reactions of **1** and comparisons to **2**. In the ^{31}P NMR spectrum of the reactions of alkali metal phenoxides with **2**, considerable amounts of disubstituted materials were observed so the rate constants for the first (k_1) and combined second (k_2) steps were determined using the SAS[8] program by integrating the coupled differential equations for both steps using k_1 and k_2 as adjustable parameters. Diflurotetrachlorocyclotriphosphazene was prepared by literature methods.[9] All other compounds were obtained by and calculations carried out by previously reported procedures.[4]

RESULTS AND DISCUSSION

The rates of reaction of equimolar quantities of sodium phenoxide (NaOPh) and $N_3P_3X_6(X = F(\mathbf{1}), Cl(\mathbf{2}))$ were obtained by GC-MS using selective ion monitoring of phosphazene reactants or products and an internal standard.[10] The half of the reaction of **2** at −15°C is 191 min. The reaction of **1** under the same condition is complete before the reaction can be quenched. The $t_{1/2}$ for **1** at −55°C is 110 min., i.e., the reaction of **1** is significantly faster than that of **2**. The n-propylamine reactions of **1** and **2** studied by Moeller[5] were reinvestigated using ^{31}P NMR spectroscopy. The order of reactivity of **2** greater than **1** previously observed[5] was confirmed in the propylamine system. A qualitative intermolecular competition study involving equimolar quantities of **1** and **2** shows exclusive reaction of **1**. In an intramolecular competition study, the reactions of 2.2-$N_3P_3F_2Cl_4$(**3**) with an equimolar amount of NaOPh proceeds by exclusive attack at the fluorinated phosphorus center followed by reattack of the displaced fluoride ion at the chlorinated phosphorus center ultimately providing 2,4,2^1-$N_3P_3F_2(OPh)Cl_3$.[10] Having established that the relative rates of reaction of **1** and **2** vary with the identity of the nucleophile,[10] we proceeded to explore the mechanistic details of the reaction of the alkai metal phenoxides with **2**.

Computational methods were employed to confirm the expected associative pathway in the reactions in question. Energies of the reactants, products and intermediates (associative vs dissociative) for the reactions of **1** and **2** with the methoxide ion were estimated using DFT calculations with a self-consistent isodensity continuum model with the dielectric constant of THF to approximate solvent stabilization. In each cases, the five coordinate intermediate for the associative process is energetically favored.

The kinetics of the reaction of LiOPh with **2**, in THF were studied as a function of temperature. The activation parameters for the first and second phenoxide addition were obtained. The formation of the transition state is endothermic reflecting the steric barrier to the incoming nucleophile in an associative process. The entropy of activation is positive reflecting solvent release from the LiOPh species. The entropy of activation of reactions of amines with **2** is negative and reflects the role of the HCl formation in the transition state.[2,11,12]

The role of the solvent was explored by determination of the kinetics of the reaction NaOPh was **2** in THF and diethyl ether. An increase of approximately two orders of magnitude in both the rates of the first and second addition of phenoxide was observed on going from the less polar(diethyl ether) to more polar (THF) solvent. The origin of this effect may be attributed to two effects. The first is the expected stabilization of the polar transition state by solvation. Of greater importance, is the role of solvent in aggregation of metal alkoxide clusters. Typically, metal alkoxides are at least tetramers in solution.[13] Lower degrees of aggregation to the kinetically active species are promoted by stronger solvation.

The role of the counter ion in the kinetics of the reactions of MOPh(M^+ = Li; Na,K) with **2** in THF was also examined. The rates increased in the order $Li^+ < Na^+ < K^+$. This order is opposite the order of lattice energies for the MCl salts. This observation suggests that metal chloride formation is not a significant contributor to the transition state, which is in contrast with reactions of amine in which HCl formation is rate determining. The observed order of reactivity is consistent with alkali phenoxide cluster deaggreation playing a role in the rate of reaction. This effect was confirmed by running the reaction in the presences of a crown ether that resulted in an increase in rate by a factor of 33.8.

The reaction mechanism for the addition of metal phenoxides to cyclotriphosphazenes can be envisioned in two parts. A rapid preequilibrium in which the tetrameric (or higher) alkali metal phenoxide is in equilibrium with monomeric or dimeric (kinetically active) species. The transition state involving the barrier of this kinetically active substrate adding to the electrophilic four coordinate phosphorus center to give a five coordinated intermediate giving rise to the greater rate of reaction of **1** over **2**. This situation, i.e., the transition state before the intermediate, is in contrast where the transition state involving HCl formation occurs after the intermediate. This model adds clarity to the understanding of the reactivity of phosphorus(V) in these systems and in phosphorus chemistry in general.

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