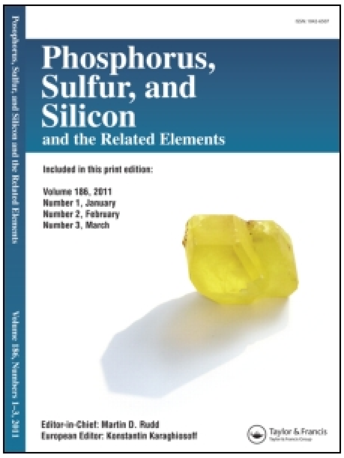
This article was downloaded by:
On: *28 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

New Insights into the Mechanistic Factors Controlling the Reactivity of Cyclotriphosphazenes

Amy S. Freund; Michael Calichman; Christopher W. Allen

To cite this Article Freund, Amy S. , Calichman, Michael and Allen, Christopher W.(2001) 'New Insights into the Mechanistic Factors Controlling the Reactivity of Cyclotriphosphazenes', Phosphorus, Sulfur, and Silicon and the Related Elements, 168: 1, 163 — 168

To link to this Article: DOI: 10.1080/10426500108546548

URL: http://dx.doi.org/10.1080/10426500108546548

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Phosphorus Sulfur and Silicon, 2001, Vol. 168, pp. 163-168
Reprints available directly from the publisher
Photocopying permitted by license only

New Insights into the Mechanistic Factors Controlling the Reactivity of Cyclotriphosphazenes

AMY S. FREUND, MICHAEL CALICHMAN
and CHRISTOPHER W. ALLEN

Department of Chemistry, University of Vermont, Burlington, VT 05405–0125, USA

Ab initio and density functional calculation on $(X_2PN)_3$(X=F(**1**), Cl(**2**)) show a significantly greater positive change on the phosphorus atoms of the fluorophosphazene which suggest that **1** should be a better electrophile than **2**. Qualitative kinetic studies using ^{31}P NMR spectroscopy show that, in agreement with previous work, **2**reacts faster than **1** with n-propylamine. When sodium phenoxide (NaOPh) was employed as the nucleophile, the reaction of **1** is much faster than that of **2**. Quantitative kinetic data using GC-Mass Spectrometry with selective ion monitoring was obtained for reactions of the phenoxide ion with **1**and **2**. Direct, intermolecular competition reactions of **1** and **2** with NaOPh show a preference of over 75% for attack on **1**. An intramolecular competition process utilizing the reaction of NaOPh with 2,2,-$N_3P_3F_2Cl_4$, gave the 2,2-$N_3P_3F(OPh)Cl_4$ derivative and the unexpected product, 2,4-difluoro-2-phenoxytrichlorocyclotriphosphazene, $N_3P_3F_2(OPh)Cl_3$. If the intramolecular competition is carried out in the presence of LiBr, $N_3P_3F_2(OPh)Cl_3$ is not observed. At the level of bis substitution of **1**, the phosphorus decoupled ^{19}F NMR spectrum of the $N_3P_3F_4(OPh)_2$ isomeric mixture shows that the cis non-geminal isomer is formed in a slight preference over the trans isomer.

Keywords: cyclophosphazenes; mechanisms of phosphazenes; mo calculations; NMR

INTRODUCTION

Inorganic ring systems exhibit a wide diversity of chemical behavior. Within this family of molecular systems, the cyclophosphazenes have the largest number of known reactions.[1-3] In addition, the range of regio- and stereochemical pathways available in substitution reactions of the cyclophosphazenes is the most complex of any inorganic ring system.[3] While synthetic and product distribution studies are extensive, publication of detailed mechanistic information has been sporatic. Early studies of Moeller [4] and Shaw [5] followed by the elegant work of Goldschmidt [6] and Krishnamurthy [7] have provided a comprehensive picture of the factors operative in the reactions of amines with chlorocyclophosphazenes. The mechanistic models derived from these studies have often been tacitly assumed to be operative in the reactions of other nucleophiles with the cyclophosphazenes. Based on the early work of Moeller [4] involving kinetics of the reactions of n-propylamine with the halocyclotriphosphazenes, $(NPX_2)_3$ [X=F(**1**), Cl(**2**), Br(**3**)], it has been assumed for nearly forty years that, in general, the rates of reaction follow the order **3**>**2**>**1**. It was shown that the entropy of activation associated with the departure of the halide ion is rate controlling in the propylamine reactions. However, it is often assumed that the rates also follow the ease of phosphorus-halogen bond breaking i.e. PBr>PCl>PF. In this investigation, we have explored the reactions of the phenoxide ion with **1**, **2**, and the mixed chlorofluorocyclotriphosphazene, 2,2-$N_3P_3Cl_4F_2$(4) as a test of the assumption described above.

RESULTS AND DISCUSSION

We have utilized ab initio (HF/6-31G*) and density functional (B3PW91/6-31G*) calculations to explore issues such as structure and charge distribution in the cyclophosphazenes and their derivatives. Applications of ab initio methods in this area are known [8] but the density functional approach has only recently attracted attention.[9] The calculated charge on the phosphorus atoms in **1** (2.54) is significantly greater than that on the corresponding center in **2** (1.84). This suggests that the phosphorus atoms in **1** should be more susceptible to nucleophiles than those in **2**. The initial approach to this question employed ^{31}P NMR to monitor the conversion of **1** and **2** to $N_3P_3X_5OPh$ (X=F(**5**)), Cl(**6**)) upon treatment with sodium phenoxide (NaOPh). At ambient temperature, after 5 minutes 30% of **6** compared to 50% of **5** was obtained. If the reactions of n-propylamine were examined 36% of **2** was consumed but only 15% of **1**. The complexity of the ^{31}P NMR spectrum of the **1**, **5** mixture lead to development of GC -mass spectrometry with selective ion monitoring as a more suitable technique for kinetic studies. The reaction of **2** with NaOPh has a half life of 196 min (at - 15 °C) while for the corresponding reaction of **1** a half life of 5.7 min (at - 45 °C) was noted. These observations clearly demonstrate that the relative rates of reactivity of

1 and **2** depend on the nature of the nucleophile with **2** reacting faster with amines and **1** reacting faster with aryloxides.

Inter- and intramolecular competition reactions were conducted. The ^{31}P NMR spectrum of an equimolar mixture of **1**, **2**, and NaOPh showed that after 10 minutes over 75% of **5** and only 5% of **6** were obtained. This clearly demonstrated the preference for attack at the phosphorus center of **1** over **2**. In order to examine the selectivity of attack within the same molecule, the reactions of **4** were examined. Density functional calculations show that the structural parameters for **4** resemble a superposition of **1** and **2**. The charges on the $\equiv PF_2$ (2.55) and $\equiv PCl_2$ (1.83) are very similar to those in **1** and **2** respectively and suggest that the $\equiv PF_2$ center should be the preferential site of attack for the phenoxide ion. The expected product of the equimolar reaction of **4** and NaOPh is 2, 2′-$N_3P_3Cl_4F(OPh)$ (**7**). When the reaction is carried out, one obtains a mixture of unreacted **4**, **7** and the unexpected 2,4-difluoro-2-phenoxytrichlorocyclotriphosphazene 2,2′,4-$N_3P_3Cl_3F_2(OPh)$ (**8**). The non-geminal disposition of the fluorine atoms in **8** indicates the occurrence of a formal geminal to non-geminal rearrangement. This is a rare event in phosphazene chemistry with the reaction of 2,2-$N_3P_3Cl_4(NH_2)_2$ with sodium alkoxides being the only other known example.[10] The reaction was repeated in the presence of LiBr (as a fluoride ion trap) to test for the role of free fluoride ion in the formation of **8**. Under these conditions only **7** was obtained. These observations along with the absence of chloride/fluoride exchange in the competition reaction of 1, 2 and NaOPh suggests that the reaction involves displacement of a fluoride ion in 4 by phenoxide and migration of the fluoride ion with the solvent cage to displace a chloride ion from a $\equiv PCl_2$ center. Both the inter- and intramolecular competition reactions show the preference for attack by the phenoxide ion at a $\equiv PF_2$ center. A model involving initial formation of a stable five coordinate intermediate being the rate controlling step in the substitution reactions involving the phenoxide ion allows one to rationalize the observed differences between 1 and 2.

The reaction of 1 with 2 moles of NaOPh gives rise to a mixture of non-geminal $N_3P_3F_4(OPh)_2$ isomers. The immense complexity of the ^{31}P and ^{19}F NMR spectra prohibits direct assignment of the isomeric composition. Phosphorus decoupling of the ^{19}F NMR reduces the spectrum to a composite of A_2B_2 (trans) and ABC_2 (cis) systems. The AB and A_2 components are clearly recognizable and integration leads to assignment of the cis isomer as being in slight excess over the trans species. There is also a small cis preference on going from $N_3P_3F_4(OPh)_2$ to $N_3P_3F_3(OPh)_3$. The counterintuitive cis preference observed in reactions of 1 and 2 with organooxy anions which have π electron rich organic moieties can be understood in terms of an interaction of the electron rich incoming nucleophile with the highly polarized aryloxy substituent on the phosphazene. This alignment leads to a preference for cis attack.

ACKNOWLEDGEMENT

The support of this research by the National Science Foundation EPSCoR program (EPS-9874685) is gratefully acknowledged.

References

[1] H.R. Allcock, *Phosphorus-Nitrogen Compounds*, Academic Press, New York (1972).

[2] C.W. Allen in *The Chemistry of Inorganic Homo-and Heterocycles*, Eds. I. Haiduc and D.B. Sowerby, Academic Press, London, Vol. 2., Chp. 20, 501 (1987).

[3] C.W. Allen, *Chem. Rev.*, **91**, 119 (1991).

[4] T. Moeller and S.G. Kokalis, *J. Inorg. Nucl. Chem.*, **25**, 1397, (1963).

[5] R.A. Shaw, *Z. Naturforsch.*, **31B**, 641 (1967).

[6] J.M.E. Goldschmidt and E. Licht, *J. Chem. Soc., Dalton Trans.*728, (1972).

[7] K.V. Katti and S.S. Krishnamurthy, *J. Chem. Soc., Dalton Trans.*285 (1985).

[8] M. Breza, *Polyhedron*, **19**, 389 (2000).

[9] A. Sundermann and W.W. Schoeller, *Inorg. Chem.*, 38, 6261 (1999).

[10] J.K. Fincham and R.A. Shaw, *Phosphorus, Sulfur Silicon*, **41**, 317 (1989).