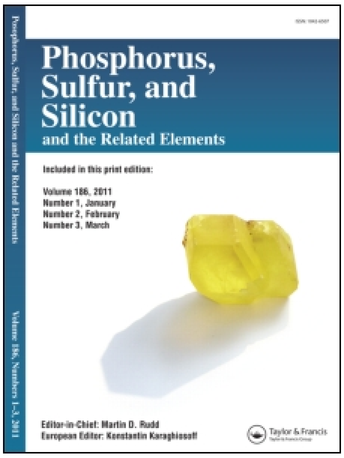

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K. V. Katti[a]; S. S. Krishnamurthy[a]
[a] Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India

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KINETICS OF THE AMINOLYSIS REACTIONS OF CHLOROCYCLOTRIPHOSPHAZENES—CHANGE-OVER FROM A $S_N2(P)$ TO A $S_N1(P)$ MECHANISM

K. V. KATTI and S. S. KRISHNAMURTHY*

Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India

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A change-over from $S_N2(P)$ to $S_N1(P)$ mechanism is established for the chlorine replacement reactions of halogenocyclophosphazenes; this mechanistic change-over helps in rationalising the diverse findings reported for this class of reactions.

Aminolysis reactions of halogenycyclophosphazenes provide examples for nucleophilic substitution reactions at a four-coordinate P(V) center whose importance in biochemical processes has been recognized.[1] As a result of numerous synthetic investigations of the aminolysis reactions of halogenocyclophosphazenes, several conclusions have emerged regarding the interplay of steric and electronic effects relating to the nucleophile and the substituent in determining the halogen replacement pattern.[2-4] Detailed kinetic studies are needed for understanding the mechanisms of these reactions and earlier attempts in this direction are limited to the replacement of the first and second chlorine atoms from hexachlorocyclotriphosphazene($N_3P_3Cl_6$) by various amines.[2,5,6] We have initiated a detailed kinetic study of the subsequent stages of chlorine replacement by determining the rates of the following reactions [Eqs. (1–4)].

$$N_3P_3(OPh)_5Cl + 2H_2NMe \rightarrow N_3P_3(OPh)_5(NHMe) + MeNH_3^+Cl^- \qquad (1)$$

$$N_3P_3(OPh)_5Cl + 2HNMe_2 \rightarrow N_3P_3(OPh)_5(NMe_2) + Me_2NH_2^+Cl^- \qquad (2)$$

$$\underset{2\text{-}trans\text{-}4\text{-}}{N_3P_3(NMe_2)_2Cl_4} + 2HNMe_2 \rightarrow \underset{2\text{-}trans\text{-}4,6\text{-}}{N_3P_3(NMe_2)_3Cl_3} + Me_2NH_2^+Cl^- \qquad (3)$$

$$\underset{2\text{-}trans\text{-}4,6\text{-}}{N_3P_3(NMe_2)_3Cl_3} + 2HNMe_2 \rightarrow \underset{2\text{-}cis\text{-}4,6,6\text{-}}{N_3P_3(NMe_2)_4Cl_2} + Me_2NH_2^+Cl^- \qquad (4)$$

The preliminary results of this investigation which has led to the observation of a $S_N1(P)$ mechanism for the first time in cyclophosphazene chemistry are reported in this communication.

EXPERIMENTAL

The chlorocyclophosphazenes were prepared and purified as described in the literature.[7,8] Methyl cyanide and the amines were distilled and dried prior to use.[5] The method of "separate bulbs" was employed for the kinetic studies in methyl cyanide in the temperature range 0–40°C.[5(b)] The progress of the reactions [(1) – (4)] were followed by estimating the amine hydrochloride at periodic intervals by potentiometric

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*Author to whom all correspondence should be addressed.

TABLE 1

Kinetic data for reaction (1) in MeCN

Temp/ °C	First order rate constant k_1/S^{-1} 30	35	40	$\Delta H^{\ddagger}$ kJ mol^{-1}	$\Delta S^{\ddagger}$ J K^{-1}mol^{-1}
	$(1.13 \pm 0.02) \times 10^{-4}$	$(1.35 \pm 0.01) \times 10^{-4}$	$(1.63 \pm 0.01) \times 10^{-4}$	24.7 ± 1	-214 ± 1

titration with a standard $AgNO_3$ solution.[5] The products of the kinetic runs were carefully identified in all the four reactions using TLC and GLC techniques[9] and ^1H NMR spectroscopy.[8] For reactions (3) and (4) the yield of the other geometrical isomer, viz., 2-*cis*-4,6-$N_3P_3Cl_3(NMe_2)_3$ or 2-*trans*-4-$N_3P_3Cl_2(NMe_2)_4$ respectively was <5%.

The order of the reactions, rate constants and activation parameters were evaluated by standard procedures.[5] Kinetic data for reaction (1) are given in Table 1.

The second order rate constants (k_2) for reaction (3) in methyl cyanide at 0,15 and 30°C are 1.08 ± 0.01, 1.58 ± 0.02 and 2.21 ± 0.01 dm^{3}mol^{-1}s^{-1} respectively. The enthalpy ($\Delta H^{\ddagger}$) and entropy ($\Delta S^{\ddagger}$) of activation for this reaction are 14 ± 1 kJ mol^{-1} and -196 ± 4 J K^{-1}mol^{-1} respectively.

DISCUSSION

The kinetic data for reactions (1), (2) and (4) fit into a first order rate law and the reaction rates depend only on the phosphazene concentration. These reactions clearly proceed by a $S_N1(P)$ mechanism involving the ionisation of the halide as the rate determining step. This is the first experimental evidence for an $S_N1(P)$ mechanism in phosphazene chemistry, although such a mechanism has been postulated by earlier workers for the replacement of the last chlorine atom in the aminolysis reactions of chlorocyclophosphazenes.[2,4] The reaction of 2-*trans*-4-bis(dimethylamino) tetrachlorocyclotriphosphazene with dimethylamine to yield 2-*trans*-4,6-tris(dimethylamino)trichlorocyclotriphosphazene [reaction (3)] follows an overall second order rate law and is first order with respect to each of the reactants. A bimolecular $S_N2(P)$ mechanism involving a penta-coordinate phosphorus intermediate is in accord with the kinetic data.[5,6] This reaction is $\sim 10^4$ times faster than the subsequent stage of chlorine replacement [reaction (4)] which occurs via a dissociative $S_N1(P)$ pathway.

The enthalpies of activation ($\Delta H^{\ddagger}$) observed for reactions (1), (2) and (4) (19–25 kJ mol^{-1}) do not differ markedly despite the structural variations in the phosphazene substrates and the reacting nucleophiles. This observation is in accord with the dissociative $S_N1(P)$ mechanism which is subject to much less steric effect compared to the associative $S_N2(P)$ pathway.[5(b),6(b),10] The large negative values of entropies of activation ($\Delta S^{\ddagger}$) for these reactions can be attributed[10] to the efficient solvation of the phosphazenium ion presumably as a result of the extensive delocalization of its positive charge.[11]

It is interesting to note that a sharp change-over from a $S_N2(P)$ to a $S_N1(P)$ mechanism occurs on going from the tris to the tetrakis-stage of chlorine replacement in the reaction of hexachlorocyclotriphosphazene with dimethylamine [reactions (3) and (4)]. This observation can be rationalized in terms of the steric requirements of the transition states involved in $S_N2(P)$ and $S_N1(P)$ mechanisms[11,12] and the mesomeric electron release from the amino substituent into the phosphazene ring.[2] A mechanistic change-over from $S_N2(P)$ to $S_N1(P)$ can explain the following diverse findings on the aminolysis reactions of chlorocyclophosphazenes: (a) the geminal directing influence of triphenylphosphazenyl (—$NPPh_3$) substituent on a secondary amino nucleophile particularly at the bis and subsequent stages of chlorine replacement and the non-isolation of a derivative of $N_3P_3Cl_3(NPPh_3)R_2$ (R = NMe_2, NEt_2, or NC_5H_{10}) containing a $\equiv PCl(NPPh_3)$ group,[3,13] (b) the prevalence of pronounced solvent effects in the reaction of $N_3P_3Cl_4(NEt_2)_2 + 2NHEt_2 \rightarrow N_3P_3Cl_3(NEt_2)_3$ and their absence in the reactions of $N_3P_3Cl_3R_3 + 2RH \rightarrow N_3P_3Cl_2R_4$

($R = NMe_2$, NEt_2 or NC_5H_{10}),[15] (c) the preponderance of nongeminal products at the bis stage and the exclusive formation of geminal products at the tetrakis stage of chlorine replacement in the reactions of hexachlorocyclotriphosphazene with ethylamine and isopropylamine[16] and (d) the wide differences in the rates of ***cis-trans*** isomerizations of (dimethylamino) chlorocyclophosphazenes, $N_3P_3Cl_{6-n}(NMe_2)_n$ ($n = 2,3,4$).[17]

In conclusion, the results reported here provide the first definite experimental evidence for a change-over from a $S_N2(P)$ to a $S_N1(P)$ mechanism in the aminolysis reactions of chlorocyclophosphazenes with increasing degree of aminolysis and also demonstrate how substituent constants derived from basicity measurements can provide a basis for predicting the stage of chlorine replacement at which such a mechanistic change-over may occur.

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