Studies in Cyclophosphazenes. Part III.[1] The Kinetics of the Reactions of Chlorocyclotriphosphazenes with Methylamine in Tetrahydrofuran

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A kinetic study of the reactions of hexachlorocyclotriphosphazene and methylaminopentachlorocyclotriphosphazene with methylamine in tetrahydrofuran has been conducted at three temperatures. In conformity with the observed orders of reaction and the magnitudes of the enthalpies and entropies of activation calculated, a two-step mechanism involving the formation of an intermediate which subsequently decomposes by solvent-assisted dehydrochlorination, is proposed. This mechanism is extended by comparing the values of the activation parameters found in this study with those evaluated previously in studying the corresponding reactions with dimethylamine. The results are interpreted by considering the differences of basicity and steric requirements of the two amines in each step of the reaction.

THE aim of this study was to investigate the rates of the amination reactions of chlorocyclotriphosphazenes employing a primary amine. Several kinetic studies of these aminations have been reported with both primary [2-4] and secondary [1,5] amines, but all detailed studies refer to the latter group of compounds. Although the influence of the amine in determining the products of these reactions has been frequently studied, comparisons of the kinetics of reactions with different amines have been virtually impossible since most studies were conducted under widely differing conditions. One report [5] included a comparison of several amines based on the values of specific rate constants. However, since consideration of the activation parameters enables more meaningful elucidation of reaction mechanisms, we have determined the mechanistic influence of the nucleophile through evaluation of these parameters.

Only for methylamine (of all primary amines) have the products of the first two stages of substitution † been well characterized,[6] and thus, this system was chosen for the present study. The rates of the following reactions were determined.

$$P_3N_3Cl_6 + 2CH_3NH_2 \longrightarrow P_3N_3Cl_5NHCH_3 + CH_3NH_3^+Cl^- \quad (1)$$

$$P_3N_3Cl_5NHCH_3 + 2CH_3NH_2 \longrightarrow P_3N_3Cl_4(NHCH_3)_2 + CH_3NH_3^+Cl^- \quad (2)$$

Reaction conditions were controlled so that effectively only one chlorine atom per phosphazene molecule was displaced in each reaction. Just as in the case of dimethylamine, reaction (2) gives overwhelmingly the *trans*-isomer. Brief mention of this study has been made in a previous preliminary report.[7]

EXPERIMENTAL

Materials.—Hexachlorocyclotriphosphazene [1], methylaminopentachloro- and bis(methylamino)tetrachlorocyclo-

† ' Stages of substitution ' is used here as defined in Part II.

[1] Part II, J. M. E. Goldschmidt and E. Licht, *J. Chem. Soc.* (*A*), 1971, 2429.
[2] J. V. Bailey and R. E. Parker, *Chem. and Ind.*, 1962, 1823.
[3] T. Moeller and S. G. Kokalis, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1397.
[4] M. Yokoyama and H. Cho, *Kogakiun Diagaku Kenkyu Hokoko*, 1964, **15**, 22 (*Chem. Abs.*, 1968, **68**, 7026).
[5] B. Capon, K. Hills, and R. A. Shaw, *J. Chem. Soc.*, 1965, 4059.
[6] W. Lehr, *Z. anorg. Chem.*, 1967, **352**, 27.
[7] J. M. E. Goldschmidt and E. Licht, *Israel J. Chem.*, 1966, **4**, 2p.

triphosphazenes [8] were prepared and purified by previously described procedures. The tetrahydrofuran (THF) was purified by the method described in Part II.[1]

The gaseous amine was liberated by boiling a 25—30% aqueous solution of methylamine (BDH reagent grade); it was passed over soda-lime and dissolved directly in THF.

Apparatus.—A Coleman Metrion IV pH-meter Model 28C was used in the potentiometric chloride-ion determinations. It was fitted with silver and calomel electrodes, the latter being immersed in a saturated solution of potassium nitrate connected to the titration vessel by an agar agar–potassium nitrate bridge.

Standardized Solutions.—The cyclophosphazene and methylamine solutions used in the kinetic experiments were prepared and standardized by the previously described procedures.[1] Suitably diluted BDH–CVS solutions of sodium hydroxide, hydrochloric acid, and silver nitrate were employed in all titrations.

Again analytical grade concentrated nitric acid was found to contain roughly 10^{-4}M-chloride ion. On dilution to the concentrations used in the quenching experiments, the chloride ion was reduced to below 10^{-6}M, leading to a maximum error of 1% in the chloride-ion determination.

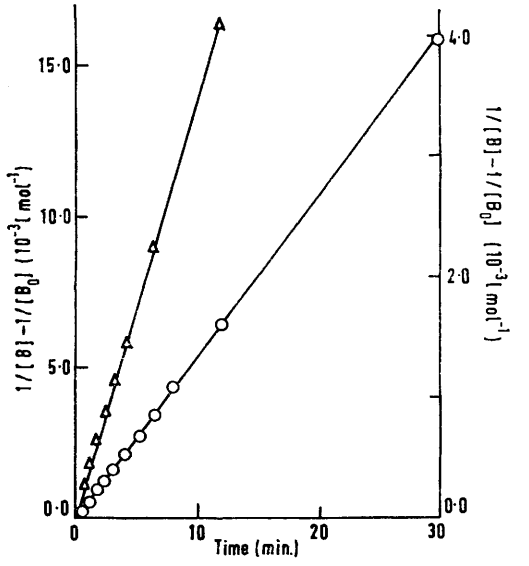
The Analytical Method.—The experimental technique of the kinetic measurements (*i.e.* the reaction vessel, the method of correcting for expansion of the THF, the procedure for timing the various processes, *etc.*) was identical to that described in Part II. However, the analytical technique for following the progress of reactions was different. At suitable intervals 10-ml samples were withdrawn from the reaction vessel and quenched by adding them to a mixture consisting of 10-ml of light petroleum and 10-ml of an aqueous solution of approximately 0·1M-nitric acid (chloride-ion free). A two-phase system resulted: the nominally organic phase consisted primarily of light petroleum and part of the THF; the aqueous phase comprised the water and the remainder of the THF. The phosphazenic starting material and the reaction product were extracted into the organic phase and the amine hydrochloride passed into the aqueous phase, the volume of which was *ca.* 13 ml. A 10-ml aliquot of the aqueous phase was introduced into the titration vessel and *ca.* 50 ml of acetone added to increase the change in potential readings at the end-point. The chloride-ion concentration was determined potentiometrically with silver nitrate. The ratio of the amount of chloride ion in the 10-ml sample to the total chloride ion in the aqueous phase was constant in every sample and was determined from the original reaction mixture. After completion of the reaction (at least one day later), two samples were taken from this solution and quenched using the standard method. A 10-ml aliquot was taken from one sample and chloride ion determined in the usual way. In the other sample, the organic and aqueous phases were separated quantitatively and then the total chloride ion was estimated in the latter phase.

RESULTS AND DISCUSSION

Details of the experiments conducted in the study of the reactions described by equations (1) and (2), as well as their results are presented in Tables 1 and 2, respectively. Average values for k_2 at each temperature studied and the activation parameters calculated from the data are presented in Table 3.

The data fitted second-order kinetics as confirmed by appropriate plots, a typical example of which is shown in the Figure. This order conforms to that found for the corresponding reactions with dimethylamine in THF.[1]

In addition to the identical orders of reaction found for reactions (1) and (2) and their counterparts involving dimethylamine, the values of the activation parameters for these sets of reactions show striking similarities as do the trends in them. Thus all the enthalpies of activation are very low and all the entropies of activation are very



Plot of $1/[B] - 1/[B_0]$ *vs.* time (min)

[B] = Concentration of methylamine at time t; $[B_0]$ = initial concentration of methylamine; ○ = graph for experiment (1) on right-hand ordinate; △ = graph for experiment (10) on left-hand ordinate

negative. Furthermore, the enthalpies and entropies of activation for the first stages of substitution are lower than the corresponding quantities in the second stages (see Table 3). These similarities suggest that the same mechanism postulated previously [1] for the reaction of chlorocyclotriphosphazenes with dimethylamine, also operates in the reactions of these substances with methylamine. According to this mechanism, the reaction takes place in two steps,* the first of which is a rapid pre-equilibrium leading to the formation of an addition complex between the amine and the cyclophosphazene. This step accounts for most of the enthalpy of activation. The second step, which is rate controlling, is associated with the bulk of the entropy of activation since it involves concerted solvation of hydrogen and chloride ions being formed in the decomposition of the intermediate. Support for the assertion that the low entropies of activation observed are associated with the formation of the two ions in the

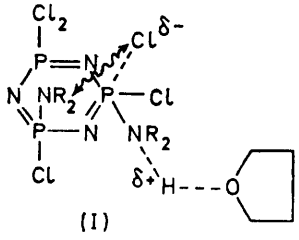
* We make the same distinction between ' steps of reaction ' and ' stages of substitution ' as made previously.[1]

[8] J. M. E. Goldschmidt and J. Weiss, *J. Inorg. Nuclear Chem.*, 1964, **26**, 2023.

rate-determining transition state comes from data reported in a recent paper,[9] in which were observed entropies of activation in the range −20 to −25 e.u. for particular cases of relatively slow, but well defined, proton-transfer processes. If it is assumed that the entropy of activation due to the solvation of the chloride ion in the processes here considered is *roughly* equal to the entropy of hydration of chloride ions, which equals −20 e.u.,[10] then the estimated total entropy of activation for the concurrent ionizations occurring in dehydrochlorination, as proposed, is the sum of the above two contributions. This calculation leads to a value of the same order of magnitude as that measured in this study. This interpretation of the mechanism notwithstanding, it is clear that for those amines investigated by us, primary amines resemble secondary amines in their mode of reaction.

Besides the above general conclusions, further clarification of certain aspects of the proposed mechanism and of the differences of reactivity of the amines studied is possible from more detailed examination of the activation parameters.

Considering first the mechanism itself; in Part II the increased entropy of activation for the second stage of substitution was ascribed to two chief causes. The first is the effect of ground-state solvation of the departing chloride ion because of its greater negative charge resulting from electron donation of the non-bonding electron pair of the substituent amine to the ring. This donation was first proposed by Becke-Goehring and her coworkers [11] and was confirmed by Bullen's bond-length and bond-angle measurements.[12] The second cause is participation of the amine substituent in solvation of the released chloride ion through a 2,4-interaction as indicated by the wavy line in the transition-state structure (I).



(I)

The planar structure, as drawn, is probably an oversimplification. Considering the known flexibility of the phosphazene ring,[13] puckering of it to give a chair-

TABLE 1

Details of the kinetic runs for the reaction: $P_3N_3Cl_6 + 2H_2NMe \longrightarrow P_3N_3Cl_5NHMe + H_3NMe^+Cl^-$

Expt.	Initial conc. of $P_3N_3Cl_6 \times 10^5$M	Initial conc. of $H_2NMe \times 10^5$M	% Reaction covered	Temp. (°C)	k_2 (l mol^{-1} s^{-1})
(1)	8·00	16·00	88	30	23·00 ± 0·25
(2)	13·50	13·50	79	30	23·00 ± 0·48
(3)	12·40	17·30	82	30	23·50 ± 0·75
(4)	7·82	15·65	68	20	21·33 ± 0·32
(5)	17·70	17·70	75	20	20·97 ± 0·38
(6)	15·60	20·00	81	20	21·22 ± 0·28
(7)	7·80	15·60	76	10	19·80 ± 0·28
(8)	17·80	17·80	72	10	19·88 ± 0·22
(9)	15·55	18·50	70	10	19·83 ± 0·27

TABLE 2

Details of the kinetic runs for the reaction: $P_3N_3Cl_5NHMe + 2H_2NMe \longrightarrow P_3N_3Cl_4(NHMe)_2 + H_3NMe^+Cl^-$

Expt.	Initial conc. of $P_3N_3Cl_5NHMe \times 10^4$M	Initial conc. of $H_2NMe \times 10^4$M	% Reaction covered	Temp. (°C)	k_2 (l mol^{-1} s^{-1})
(10)	5·36	10·72	81	30	2·22 ± 0·05
(11)	6·72	6·72	73	30	2·25 ± 0·07
(12)	5·36	10·72	76	20	1·78 ± 0·05
(13)	6·72	6·72	68	20	1·88 ± 0·12
(14)	4·36	7·32	75	20	1·75 ± 0·07
(15)	5·36	10·72	78	10	1·45 ± 0·05
(16)	6·72	6·72	86	10	1·48 ± 0·03

TABLE 3

Summary of average results calculated for data in Tables 1 and 2

Data for Table	k_2 at 30°	k_2 at 20° (l mol^{-1} s^{-1})	k_2 at 10°	ΔH^* Enthalpy of activation (kcal/mol)	ΔS^* Entropy of activation (e.u.)
1	23·17 ± 0·58	21·17 ± 0·37	19·83 ± 0·27	0·7 ± 0·4 (1·7 ± 0·5) [a]	−49 ± 1·5 (−47 ± 2) [a]
2	2·23 ± 0·07	1·80 ± 0·10	1·47 ± 0·05	3·0 ± 0·8 (5·1 ± 0·6) [a]	−46 ± 3 (−38 ± 2) [a]

[a] The values in parentheses are for the corresponding reactions with dimethylamine in THF.[1]

[9] D. F. Caldin, A. Jarczewski, and K. T. Leffek, *Trans. Faraday Soc.*, 1971, **67**, 110.

[10] K. B. Harvey and G. B. Porter, 'Introduction to Physical Inorganic Chemistry,' Addison-Wesley Publ. Co., Reading, Mass., 1963, p. 326.

[11] M. Becke-Goehring, K. John, and E. Fluck, *Z. anorg. Chem.*, 1959, **302**, 103.

[12] G. J. Bullen, *J. Chem. Soc.*, 1962, 3193.

[13] N. L. Paddock in 'Developments in Inorganic Polymer Chemistry,' eds. M. F. Lappert and G. J. Leigh, Elsevier, Amsterdam, 1962, p. 102.

configuration, bringing the substituent and the departing chloride ion in the axial positions closer, is reasonable. In addition, the results of recent studies of the equilibrium between *cis*- and *trans*-bis(dimethylamino)tetrachlorocyclotriphosphazenes [14] provide more direct evidence of the existence of puckered phosphazene rings in solutions of these types of compounds. This solvation effect by the substituent amine should result in only a small loss in the degrees of freedom of the system compared with a far greater loss of freedom by the system as a whole on solvation by solvent molecules. Assuming displacement with inversion, this substituent solvating effect can only come about if the ring is attacked from the side opposite the substituent, in a reaction that leads to the *trans*-isomeric product. Attack from the same side as the substituent, leading to the *cis*-isomer would not be kinetically aided by this substituent solvating effect, and the entropy of activation for this process would be roughly equal to that found in the first stage of substitution. This rationalization for the known predominance of the *trans*-isomer was briefly hinted at in Part II. Support for these contentions comes from the following considerations. It is known that under the conditions employed in the kinetic experiments the *cis*-isomer comprises *ca.* 10% of the total product in these reactions,[15] and, therefore, k_2 (*cis*) can be estimated as k_2 (*trans*)/10. Furthermore, assuming that the enthalpy of activation, related chiefly to the attack of the amine on the substrate, is equal for both *cis*- and *trans*-attack then the entropy of activation for the *cis*-reaction can be calculated, and as suggested previously it should not differ greatly from the value found in the first stage of substitution. These views conflict with those of Keat and Shaw [16] who postulate the '*cis*-effect' involving greater repulsion to attack from the same side of the ring as the substituent, implying increased enthalpy of activation for *cis*-attack. On these assumptions, the calculation for the reaction of methylaminopentachlorocyclotriphosphazene with methylamine to produce the *cis*-isomer gives an estimated value of the entropy of activation of −51 e.u., compared with a measured value of $-49 \pm 1{\cdot}5$ e.u. in the first stage of reaction. Making the same assumptions and employing the data contained in Part II, the estimated value of the entropy of activation for the reaction of dimethylaminopentachlorocyclotriphosphazene with dimethylamine leading to the *cis*-isomer is −45 e.u. compared with a value of -47 ± 2 e.u. in the first stage of that reaction. The agreement is considered satisfactory in view of the assumptions made. The fact that the data agree for *both* reactions indicates that changes in the rate-controlling entropy of activation in the second dehydrochlorination step, rather than changes in the enthalpy of activation associated with the formation of the intermediate in the first step, are primarily responsible for the stereoselectivity of these reactions. A corollary of this theory concerns the higher value of the enthalpy of activation in the second stage, compared with the first stage. This increase was previously ascribed [1] to one cause only, *viz.* the phosphorus atom at which the displacement occurs is less electrophilic because of the increased negative charge caused by the amine substituent, as explained above. However, in addition, the proximity of the substituent to the chloride ion being expelled must give rise to an enthalpic change—presumably an increase—in the second transition state and this also contributes to the rise in enthalpy of activation in the second stage of substitution.

Now let us compare the values of the activation parameters for the reaction of hexachlorocyclotriphosphazene with methylamine with those obtained in the study of the same substrate with dimethylamine. Since reactions of one substrate with different amines are being considered, any observed differences can only be ascribed to differences in the amines. The enthalpy of activation for the reaction with methylamine equals $0{\cdot}7 \pm 0{\cdot}4$ kcal/mol, whilst the value for the reaction with dimethylamine is $1{\cdot}7 \pm 0{\cdot}5$ kcal/mol. It is this increase in enthalpy of activation which causes the retardation of the rate of reaction on going from methylamine to dimethylamine since it completely cancels the opposing influence of the accompanying changes in the entropy of activation. Assuming relative nucleophilicities to be roughly proportional to basicities, the former amine is the weaker nucleophile, and its enthalpy of activation should be greater. The opposite effect, as measured, indicates that the steric differences between the amines are decisive. The influence of steric factors has been observed earlier both in rate [5] and in preparative studies [17] of these compounds. The identification of these steric factors with changes of the enthalpy of activation, confirming their nature, is at first sight contradictory since the rates of all these reactions are controlled by the entropy of activation. This apparent contradiction is readily resolved when it is realized that the enthalpic–steric factors chiefly influence the pre-equilibrium, *i.e.* primarily they reduce the concentration of the amine–phosphazene adduct; however, they hardly affect the rate of decomposition of this intermediate. This decomposition is the rate-determining step on account of its large, retarding, entropic contribution to the free energy of activation. Finally it should be remembered that the existence of the steric effect, coupled with the very low values of enthalpy of activation observed, are an indication of the very high electrophilicity of the phosphorus centre, a property consistent with delocalization of charge around the ring. In contrast to the almost threefold increase of enthalpy of activation, the differences of entropy of activation for the methylamine reaction ($-49 \pm 1{\cdot}5$ e.u.) and the dimethylamine reaction (-47 ± 2 e.u.) are very small. The near equality of the entropies of activation is taken as evidence for the occurrence of virtually the same process in both cases, *viz.* the solvation of the chloride and hydrogen ions being

[14] J. M. E. Goldschmidt and M. Segev, unpublished results.
[15] M. Davidor and J. M. E. Goldschmidt, unpublished results.
[16] R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 908.
[17] S. K. Ray and R. A. Shaw, *J. Chem. Soc.*, 1961, 872.

formed in the second transition state, through decomposition of the intermediate. However, the slightly differing values observed do reflect a trend found in other cases [18] which can be interpreted in terms of variations of basicity and steric requirements that weaken the phosphorus–chlorine bond, thus reducing the extent of solvation required to reach the transition state of decomposition of the intermediate. This effect results in a higher value of the entropy of activation.

With both the amines and substrates differing, it is impossible to compare the data for the second stages of reaction, as was done above for the first stages. Even potentially useful indirect comparisons that would throw light on the substituent effect are precluded by the magnitude of the errors which virtually equal the quantities being considered. Direct studies of the substituent effect are currently under investigation.

[1/877 *Received, 2nd June,* 1971]

[18] J. M. E. Goldschmidt and E. Licht, unpublished results.