245. *Cyclic Inorganic Compounds. Part I. Chlorine Exchange Reactions with the Chlorophosphonitriles.*

By D. B. Sowerby.

A kinetic investigation of radioactive chlorine exchange between chloride ion and the homologous chlorophosphonitriles, $(PNCl_2)_{3-6}$, in acetonitrile solution has been carried out. The exchange process is second order in all cases, and an S_N2 mechanism is suggested. The second order rate constants give the order of reactivity of the phosphonitriles as $P_4N_4Cl_8 > P_5N_5Cl_{10} > P_6N_6Cl_{12} > P_3N_3Cl_6$.

A VARIETY of nucleophilic reagents have been used to replace the chlorine atoms in the two lowest members (trimer and tetramer) of the chlorophosphonitrile series, but until recently there has been no attempt to study the kinetics and mechanism of such processes. Some conclusions were, however, reached from preparative experiments on the probable importance of steric and electronic effects of the substituting nucleophile, and thus the order of substitution of the chlorine atoms in hexachlorotriphosphonitrile on aminolysis,[1,2] arylation,[3] and fluorination [4] can be rationalized.

Recently, Bailey and Parker [5] have studied the kinetics of aminolysis of hexachlorotriphosphonitrile with aniline in an alcohol–benzene medium. This is a complicated

[1] Becke-Goehring and John, *Z. anorg. Chem.*, 1959, **302**, 103.
[2] Ray and Shaw, *J.*, 1961, 872.
[3] Acock, Shaw, and Wells, *J.*, 1964, 121.
[4] Chapman, Paine, Searle, Smith, and White, *J.*, 1961, 1768.
[5] Bailey and Parker, *Chem. and Ind.*, 1962, 390.

process as the phosphonitrile undergoes alcoholysis as well as aminolysis and after substitution of one chlorine atom, the successive steps are difficult to separate. However, it was possible to show that initially the reaction is of second order. The reaction between the trimeric chloride and piperidine has also been examined,[6] but the most extensive study to date has been that of Moeller and Kokalis [7] on the reaction between various halogenophosphonitriles and n-propylamine in acetonitrile.

In all these experiments, however, complications arise owing to the change in the nature of the substrate on substitution of the first chlorine atom; thus we have approached the problem of reactivity in chlorophosphonitrile systems through radioactive chlorine exchange reactions. Although these processes give only a limited amount of information when compared with a complete study of say, aminolysis, they are more easily examined and readily give unambiguous results. Here we deal with processes involving the unsubstituted chlorophosphonitriles. Subsequently, we will consider exchange processes with various partially substituted compounds.

EXPERIMENTAL

Chlorophosphonitriles.—The trimeric and tetrameric chlorophosphonitriles were commercially available materials (Albright and Wilson, Ltd.), purified to accepted melting points by recrystallization from petroleum ether and high vacuum sublimation. The pentameric and hexameric compounds were kindly provided by Dr. N. L. Paddock of the University of Manchester.

Radioactive Tetraethylammonium Chloride.—The labelled compound was prepared, either by neutralizing an aqueous solution of tetraethylammonium hydroxide with hydrochloric acid containing the required amount of radioactive hydrochloric acid, or by treating a concentrated aqueous solution of tetraethylammonium chloride with radioactive hydrochloric acid. In either case, the solution was taken to dryness in a vacuum and dried overnight in vacuum at 80°. The salt was purified by adding a filtered solution in chloroform to an excess of ether cooled to −70°. The resulting fine, white, precipitate was removed on a sintered glass disc and dried in a vacuum. Subsequently, the compound was handled only in a dry-box.

Acetonitrile.—The solvent was repeatedly distilled from P_4O_{10} until the desiccant no longer darkened (6—8 times). Finally, the anhydrous material was distilled alone.

Exchange Procedure.—Solutions of the required phosphonitrile and tetraethylammonium chloride in acetonitrile were prepared and after gaining constant temperature in a thermostat, they were mixed (zero time). After suitable time intervals, aliquots were removed from the reaction vessel and added to an excess (~8 fold) of ether at −70°. The precipitated tetraethylammonium chloride was collected on a sintered glass disc, then washed three times with anhydrous ether and dried at room temperature; it was dissolved in 10 ml. of distilled water for radioassay. The efficiency of separation varied slightly but was ~90% complete. An annular solution counter attached to conventional scaling equipment was used for radioassay. Corrections for the slight differences in efficiency of chloride separation within a run were made by converting all activities to a standard weight after estimating the chloride content of the assayed solutions with N/100-mercuric nitrate solution. The activity of the original tetraethylammonium chloride was determined for each run and usually the exchange reactions were allowed to proceed to obtain the activity at infinite time. As the rate of reaction is followed by observing the decrease in activity of the separated ionic chloride, the percentage exchange is given by $100(a_s - a_t)/(a_s - a_\alpha)$ where a_s = activity at zero time, a_t = activity at time, t, a_α = activity at infinite time.

Plots of log (100 − % exchange) against time of separation were linear with an intercept of two at zero time, showing that no exchange was induced by the separation procedure. The exchange half-life was obtained from these graphs, and the rate of reaction was calculated, in the case of hexachlorotriphosphonitrile, using the equation:

$$R = \frac{0{\cdot}693 \times 6[P_3N_3Cl_6][Et_4NCl]}{t_{\frac{1}{2}} \times \{6[P_3N_3Cl_6] + [Et_4NCl]\}}$$

The factor 6 arises as there are six equally exchangeable chlorine atoms in hexachlorotriphosphonitrile. In the case of octachlorotetraphosphonitrile, a factor 8 would be substituted. The

---

[6] Capon, Hills, and Shaw, *Proc. Chem. Soc.*, 1962, 390.

[7] Moeller and Kokalis, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1397.

temperature variation of exchange rate was obtained from reactions carried out at 0, 25, and 35°.

Data for the reactions with the trimeric chloride are given in Table 1, while Table 2 contains typical results with the higher homologues.

TABLE 1.

Exchange of ^{36}Cl between chlorine ion and hexachlorotriphosphonitrile.

Temp. (°c)	$10^2[P_3N_3Cl_6]$ (mole l.$^{-1}$)	$10^2[Et_4NCl]$ (mole l.$^{-1}$)	$t_{\frac{1}{2}}$ (sec.)
0	1·525	1·841	12,200
	1·991	1·742	10,360
	1·129	1·742	16,100
25	0·632	1·082	1,645
	1·405	1·799	840
	1·160	1·797	935
	0·907	1·797	1,060
	0·667	1·896	1,305
25	0·392	1·768	2,185
	1·033	1·848	1,020
	2·060	1·848	620
	4·167	3·696	300
	1·756	1·632	680
35	0·556	1·100	659
	0·827	1·225	488
	0·707	1·215	553

TABLE 2.

Exchange of ^{36}Cl between chloride ion and the higher phosphonitriles.

	Temp. (°c)	10^4[Phosphonitrile] (mole l.$^{-1}$)	$10^3[Et_4NCl]$ (mole l.$^{-1}$)	$t_{\frac{1}{2}}$ (secs.)
$P_4N_4Cl_8$	0	7·64	8·35	5,290
	25	5·82	8·70	480
	35	8·41	4·06	225
$P_5N_5Cl_{10}$	0	45·1	13·96	6,600
	25	20·0	6·44	940
	35	14·5	3·95	560
$P_6N_6Cl_{12}$	0	7·54	5·19	44,000
	25	10·3	6·07	2400
	35	15·1	9·79	725

TABLE 3.

Solubility of chlorophosphonitriles in acetonitrile.

	Solubility (g./1000 g. solvent)		
	0°	25°	35°
$P_3N_3Cl_6$	19·6	54·6	82·6
$P_4N_4Cl_8$	1·39	6·66	9·65
$P_5N_5Cl_{10}$	20·0	70·7	113·6
$P_6N_6Cl_{12}$	2·07	7·84	13·8

Solubility of Chlorophosphonitriles in Acetonitrile.—Quantitative solubilities of the homologous phosphonitriles were determined by evaporating, under reduced pressure, weighed amounts of saturated solutions of the phosphonitriles. The results are shown in Table 3. The very low solubilities of the tetrameric and hexameric compounds severely restricted the concentration range that could be used in the exchange processes. All solutions of the phosphonitriles in acetonitrile are non-ideal, but there is a parallel between solubility and melting point for each homologue. The results agree with observations using other solvents in which the solubility of the homologues decreases in the order pentamer $>$ trimer $\gg$ tetramer.[8] On the basis of the little data available, it is not possible to generalize on the position of the hexamer in this series.

DISCUSSION

It has been shown from conductance measurements that tetraethylammonium chloride is a strong electrolyte in acetonitrile solution,[9] and thus chloride ion is the attacking species in exchange reactions with the phosphonitriles. The variation in the rate of chlorine exchange with changes in the concentration of the phosphonitrile and tetraethylammonium chloride, in each case, shows a first-order dependence on both species. Values of the second-order rate constant together with energies of activation and log A factors are summarized in Table 4. It seems likely, therefore, that the exchange of radiochlorine in

---

[8] Paddock and Searle, "Advances in Inorganic Chemistry and Radiochemistry," Vol. 1, Academic Press, New York, 1959, p. 348.

[9] Lewis and Sowerby, *J.*, 1957, 336.

these experiments follows a bimolecular path and involves a five co-ordinate phosphorus atom in the transition state. A similar mechanism has been postulated in reactions with other chlorophosphonitriles.[5,7]

TABLE 4.

	Temp. (°c)	k_2 (sec.$^{-1}$ mole l.$^{-1}$)	E (kcal. mole^{-1})	$\log_{10} A$
$P_3N_3Cl_6$	0	$3{\cdot}03 \times 10^{-3}$		
	25	$5{\cdot}01 \times 10^{-2}$	18·3	12·1
	35	0·139		
$P_4N_4Cl_8$	0	$7{\cdot}26 \times 10^{-2}$		
	25	0·892	16·3	12·0
	35	2·29		
$P_5N_5Cl_{10}$	0	$1{\cdot}92 \times 10^{-2}$	17·0	11·9
	25	0·281		
	35	0·660		
$P_6N_6Cl_{12}$	0	$1{\cdot}39 \times 10^{-2}$		
	25	0·188	16·3	11·2
	35	0·412		

In general, solvolyses and chlorine replacement reactions with species such as phosphochloridates and phosphinyl chlorides occur by a similar mechanism.[10,11] A limited number of radiochlorine exchange reactions with phosphorus compounds have been examined kinetically. The one most similar to the chlorophosphonitrile exchanges is that involving phosphoryl chloride.[9] Exchange in acetonitrile solution is first order in both chloride ion and phosphoryl chloride. At $-20°$, the second order rate constant (k_2) is 2·06 sec.$^{-1}$ mole^{-1} l., and k_2 is calculated as 100 sec.$^{-1}$ mole^{-1} l. at 25°. Although direct comparison is not possible, the phosphoryl chloride exchange is several orders of magnitude faster than that with the triphosphonitrile. The difference lies in the lower activation energy of the phosphoryl chloride exchange process, and can probably be related to the change in electrophilicity at the phosphorus centre. In the phosphonitrile, the phosphorus atom would be expected to carry a partial positive charge, but this would not be as great as possibly expected, owing to π and π' overlap in the cyclic system.[12] Reduction of the formal positive charge on the phosphorus atom of phosphoryl chloride would not be expected to take place to the same extent.

In the unsubstituted chlorophosphonitriles, there is no evidence for kinetically different chlorine atoms. As far as can be determined with the present technique, all the chlorine atoms in each phosphonitrile exchange at the same rate. This is expected in the case of the trimeric chloride, which has a planar symmetrical structure, but differences may have been detected with the high homologues if there had been a preferential conformation of the rings in solution. It is postulated that there is great ring flexibility in the pentameric and hexameric phosphonitriles.

The rate constants in Table 4 have been calculated using the true molar concentrations of the phosphonitriles in the equation:

$$\text{Rate} = k_2[P_nN_nCl_{2n}][Et_4NCl]$$

For purposes of comparison between the members of the phosphonitrile series, it would be more convenient to express all concentrations in terms of the hypothetical $PNCl_2$ monomer. Differences in rates of exchange due to the difference in the number of chlorine atoms in the various homologues would then be removed. The rate constants based on this concentration unit can be obtained from the old values by dividing them by the degree of polymerization of the phosphonitrile. For trimer to hexamer, the values are respectively: 0·0167, 0·223, 0·056, and 0·031 sec.$^{-1}$ mole^{-1} l. at 25°. The order of the compounds, however, is not changed by using this alternative method of expressing the concentration.

[10] Dostrovsky and Halman, *J.*, 1953, 502, et seq.
[11] Grunden and Hudson, *J.*, 1962, 3591.
[12] Craig and Paddock, *J.*, 1962, 4118.

There is no simple trend in the variation of rate constant with ring size. The trimeric compound has the lowest value, and the ratios k_n/k_{trimer} using the rate constants above are 13·4, 3·35, and 1·88, respectively, for the tetramer, pentamer, and hexamer. The high value for the tetramer bears out the observation from preparative experiments that substitution reactions with the tetrameric compound occur more readily than comparable processes with the trimer. The low rate constant for the trimer is associated with the highest energy of activation in the series. Except for the hexamer, there is no significant variation in the log A factor.

The explanation offered by Moeller and Kokalis [7] for the variation in rate of aminolysis of the halogenophosphonitriles with ring size is in terms of the ease with which changes in conformation at the phosphorus atom can occur. The formation of a five-co-ordinate transition state could occur more readily with the flexible tetrameric molecule; the trimeric ring system on the other hand, is more rigid and greater and more energetic rearrangements would be required. This explanation alone is not completely satisfactory, as one would expect that the rate of exchange of the more highly flexible pentameric and hexameric phosphonitriles would be comparable, if not higher than that of the tetrameric species. The observation is, however, that the rate of exchange is markedly reduced in the case of these higher phosphonitriles. Variation in ring size of the chlorophosphonitriles as well as changing the stereochemistry at the phosphorus atoms, undoubtedly brings about changes in the electron density. The basic σ-framework of the phosphonitriles leads to a formal charge of $+1$ on each phosphorus atom, but π-bonding of any description necessarily leads to a decrease in this charge and thus to a decreased susceptibility to nucleophilic attack. Changes in electronic environment must also be considered to account for the order of reactivity of the homologous phosphonitriles. With the data presently available, it is not possible with certainty to assess separately the magnitude of the electronic and steric effects.

This research was carried out at University College, London, during the tenure of an I.C.I. Fellowship. Thanks are due to the late Professor E. D. Hughes and Professor R. S. Nyholm for facilities in the William Ramsey and Ralph Forster Laboratories, and to Professor A. W. Adamson and Drs. N. L. Paddock and M. L. Tobe for their interest and help.

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTTINGHAM. [*Received, April* 30*th*, 1964.]