104. *Kinetic Studies in the Phosphinyl Chloride and Phosphorochloridate Series. Part IV.* General Discussion.*

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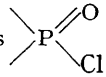
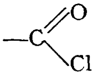
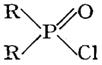
The results of the kinetic investigations reported in the three preceding papers are critically analysed, and the possible mechanism discussed. Special attention is paid to the possible existence in these reactions of a " transition complex " possessing an expanded valency shell of the phosphorus atom. No evidence could be obtained for any great stability of such a complex. The reactions studied in the previous papers are thus assumed to be simple bimolecular displacements similar to those observed with the analogous carbon compounds. The comparison of the reactions of the phosphorochloridates and phosphinyl chlorides with their carbon analogues reveals the great similarity, both qualitatively and quantitatively, of the groupings  and 

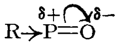
THE ability of elements of the second and higher rows of the Periodic Table to use more than four orbitals in bond formation has been invoked to explain the marked differences in the rates of hydrolysis and alcoholysis of their halides as compared with those of carbon (cf. Sidgwick, " Electronic Theory of Valency," Oxford Univ. Press; *J.*, 1924, **125**, 2672). This view assumes the formation of a relatively stable " transition complex " using an extra bonding orbital, which then undergoes decomposition by a unimolecular process. In this process the requirement of simultaneous bond breaking and bond formation, essential in the S_N2 type of mechanism, is waived, so that reaction is facilitated. The experiments described in Parts I—III were undertaken in order to test the applicability of this view to the reactions of the phosphorohalidates and related compounds.

With the possible exception of the solvolysis in formic acid and the reaction with tertiary amines, the reactions of the phosphorochloridates and phosphinyl chlorides are simple substitutions at the phosphorus atom. The kinetic analysis of these reactions provides no evidence for an S_N1 type of reaction and leads to the conclusion that the solvolyses and the second-order reactions with strong nucleophilic reagents proceed by the same mechanism. We now examine the possible routes of these reactions in the light of our evidence.

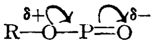
The effect of structural changes in the phosphorochloridates and phosphinyl chlorides may be understood by considering the possible interaction of the groups R with the oxygen atom in the compound (I). On account of the electronegativity difference between oxygen and phosphorus, and between chlorine and phosphorus, the phosphorus atom will carry a small positive charge and be the electrophilic centre of the molecule. Any electron release from the group R will weaken this centre. Such electron release may be caused by inductive effect in the group R, or by an electromeric effect if the group R contains unshared p-electron or π-electrons. These effects are represented in (II) and (III). Using the well-established principles governing these effects, we can arrange the groups in order of their electron release to the P atom, *viz.* : Me < Ph; Me < MeO < EtO < PrO. Reference to Table I of Part I (*J.*, 1953, 502) and Tables 2 and 3 of Part III (*loc. cit.*) shows that the rates of reaction decrease with electron accession to the phosphorus atom according to the same sequence. Thus a change from R = Me to R = OMe [in $Cl{\cdot}PMe_2O$ and $Cl{\cdot}P(OMe)_2O$] causes a 300-fold decrease in the rate of solvolysis in absolute ethanol. Similarly, a change from R = OMe to R = OPr^i causes a 5-fold decrease in the rate of solvolysis (dimethyl and di*iso*propyl phosphorochloridates) and a 3-fold decrease in the rate of reaction with di-*n*-butylamine. The effect of variation in structure on the



(I)



(II)



(III)

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* Part III, preceding paper.

reactions with negative ions is much greater (cf. Part II, *J.*, 1953, 508): the rate of reaction of diethyl phosphorochloridate with ethoxide ion is some 26 times that of the di*iso*propyl ester, while the rate of reaction of the first ester with fluoride ions is some 9 times that of the second.

The way in which the reaction rates depend upon the electron density on the phosphorus atom and the greater sensitivity of the rate of reaction with negative ions to changes in this density show clearly that the rate-controlling step involves the approach of the nucleophilic reagent to this atom (cf. Hinshelwood, Laidler, and Timm, *J.*, 1938, 848).

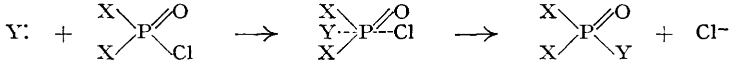
The rates of solvolysis of the esters $Cl{\cdot}PO(OR)_2$ in dry ethanol vary with R thus: $CH_2Ph > Me > Ph$, although the differences are not large. The first inequality accords with the reduced hyperconjugation of the methylene hydrogen atoms; and the second with the greater participation of the phenyl group in the electromeric effect. The situation is analogous to that in the relative strengths of *p*-substituted benzoic acids (cf. Dippy, *Chem. Reviews*, 1939, **25**, 151).

Our results are in accordance with Toy's observations (*J. Amer. Chem. Soc.*, 1948, **70**, 3882; 1950, **72**, 2065), and those by Kosolapoff and Watson (*ibid.*, 1951, **73**, 4101, 5466), that the hydrolysis of tetra-alkyl pyrophosphates is much slower than that of the corresponding anhydrides of dialkylphosphinic acid.

The view that the rate-determining step involves the approach of the reagent is supported further by the effect of structural variation of the amines in their reactions with phosphorochloridates (cf. Part III, Table 3). We have seen that the rate of sequence for various amines is in keeping with their base strength with respect to bulky reference acids. Since the base strength thus defined is determined by steric interaction between amine and acid, we conclude that in the reaction with di*iso*propyl phosphorochloidate the approach of the reagent is involved in the rate-determining step, and the reaction is then subject to steric hindrance operating between the amine and the ester. Similar reasons account for the extreme slowness of the solvolysis in *tert.*-butyl alcohol (cf. Part I, *J.*, 1953, 503).

The magnitude and direction of solvent effects give information regarding the state of electrical charge in the transition state relative to that in the reagents. Ionising solvents exert an accelerating effect in the solvolytic reactions and on the reactions with amines (cf. *J.*, 1953, pp. 503, 513). Thus, in the solvolysis of di*iso*propyl phosphorochloridate, a change from absolute ethanol to 60% aqueous ethanol increases the rate 9·4 times (Table 3, *ibid.*, p. 503), and in its reaction with di-*n*-butylamine a change from benzene to nitrobenzene causes a 100-fold increase in rate (cf. Table 4, *ibid.*, p. 513). These facts indicate that the transition state carries a higher charge than the reactants. Similarly, in the reaction of di*iso*propyl phosphorochloridate with fluoride ions, a change from absolute to 60% ethanol leads to a 6-fold decrease in rate (cf. *ibid.*, p. 508), indicating that the initial negative charge of the fluoride ion has been dispersed in the transition state (cf. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 604). The observed salt effects (*ibid.*, pp. 504, 509, 513) are also consistent with these conclusions.

From the fact that *iso*propyl phosphorofluoridate reacts slower than its chlorine analogue and that the corresponding iodide reacts faster (McCombie, Saunders, and Stacey, *J.*, 1945, 380, 921), one can conclude that the bond between the halogen and the phosphorus atom is also involved in the transition state. Taking all these facts together, we can write for the reactions between the phosphorochloridates and nucleophilic reagents the usual bimolecular scheme of reaction with bond-making influences predominating:



A similar conclusion has been reached (Hughes, *Quart. Reviews*, 1951, **5**, 268) with respect to the mechanisms of solvolysis of triphenylsilyl fluoride. In cases where the reagent Y is a neutral molecule carrying a hydrogen atom, *e.g.*, water, alcohols, secondary and primary amines, the question may arise whether the elimination of the proton is involved in any rate-determining stage of the reaction. An attempt to answer this question was made by comparing the rates of solvolysis in D_2O and in ordinary water (Table 3, *J.*, 1953, 503), but the slightly slower rate in D_2O could be accounted for by the slightly different solvent properties. A further test was carried out by observing the rates of the reaction of di*iso*propyl phosphorochloridate with di-*n*-butylamine in the presence of added triethylamine. Here also no significant effect of the added base was noted. Had proton removal been involved in a rate-determining step, considerable effects should have been observed in both the experiments described above. We therefore conclude that in solvolyses and in reactions with primary and secondary amines, the proton of the reagent is eliminated in a fast step following the rate-controlling bimolecular displacement of the halogen atom.

There is only little support for the " addition complex " theory in the evidence presented in these papers. The reactions could still be presented by the following sequence, although somewhat less satisfactorily :

$$\mathrm{Y + PX} \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \mathrm{YPX} \xrightarrow{k_3} \mathrm{YP + X^-}$$

whence $-\mathrm{d[PX]/d}t = k_2k_3[\mathrm{Y}][\mathrm{PX}]/(k_1 + k_3)$. Now, if $k_1 \ll k_3$ the reaction reduces to the normal bimolecular reaction discussed above. However, if $k_3 \ll k_1$, the reaction can be written $-\mathrm{d[PX]/d}t = Kk_3[\mathrm{Y}][\mathrm{PX}]$, where $K = k_2/k_1$.

Now, increasing electron accession to the phosphorus atom will reduce the value of K and increase k_3, so the resulting effect on the reaction will depend on the relative magnitude of these effects and in any case will be reduced by partial cancellation. In order to account for the observed direction of the effect, it is necessary to assume that the effect on K will predominate. It is impossible to give a definite answer to this point. However, the apparently reasonable magnitude of the retardation effect appears to favour a straightforward bimolecular reaction. Further doubt on the validity of the " addition complex " mechanism has been cast by Sommer and his co-workers (*J. Amer. Chem. Soc.*, 1951, **73**, 5130). It appears therefore that the mechanisms of the reactions of phosphorochloridates and phosphinyl chlorides are identical with those of analogous carbon compounds, with no new effects due to the position of the phosphorus atom in the periodic table.

Having established the similarity of mechanisms of phosphorus and carbon compounds, we proceed to compare analogous compounds in greater detail. Perhaps the most surprising result of such a comparison is the great similarity of the groups $>\mathrm{PCl{:}O}$ and $-\mathrm{CCl{:}O}$, not only in the relative effect of changes in reaction variables on the rate of reaction, but also in the absolute values of the rate constants of the two series of compounds. Phosphorochloridates $\mathrm{Cl{\cdot}PO(OR)_2}$ may be regarded as the analogues of chloroformates ($\mathrm{Cl{\cdot}CO_2R}$) and the phosphinyl chlorides ($\mathrm{Cl{\cdot}PR_2O}$) as the analogues of carboxylic acid chlorides ($\mathrm{R{\cdot}COCl}$). The rates of methanolysis for a number of alkyl chloroformates (Leimu, *Ber.*, 1937, **70**, 1940) are given in Table 1 together with our results for the ethanolysis of the analogous phosphorochloridates.

TABLE 1. *Kinetics of the solvolysis of alkyl chloroformates and dialkyl phosphorochloridates at 25°.*

	Chloroformates [a]			Phosphorochloridates [b]		
	$k \times 10^4$, sec.$^{-1}$	E_A, kcal./mole	$10^{-6}PZ$, sec.$^{-1}$	$k_1 \times 10^4$, sec.$^{-1}$	E_A, kcal./mole	$10^{-6}PZ$, sec.$^{-1}$
Me	1·64	15·5	4·1	5·3	12·0	0·25
Et	0·90	15·8	3·7	1·7	13·4	1·2
$\mathrm{Pr^i}$	0·41	16·3	4·1	0·61	12·8	0·16

[a] Leimu (*loc. cit.*), in methanol. [b] Calc. from authors' results (*J.*, 1953, 502).

It is evident that the effect of substituents on the rates of reaction is in the same direction in the two series and only slightly more pronounced for the phosphorus compounds. It is seen that, after allowance for the difference in media, the rates of solvolysis of the phosphorus compounds are only some 4—16 times greater than those of the analogous carbon compounds. A direct comparison can be made in the case of the *iso*propyl compound where the rate of methanolysis of the phosphorochloridate is exactly 4 times that of the chloroformate (cf. *J.*, 1953, **503**).

The rates of solvolysis of acetyl and benzoyl chlorides have been measured by Norris (*J. Amer. Chem. Soc.*, 1935, **57**, 1416) and by Branch and Nixon (*ibid.*, 1936, **58**, 492, 2499), whose results are compared with those for the analogous phosphinyl chlorides, *viz.*, dimethyl-and diphenyl-phosphinyl chlorides, in Table 2. Examination of these data indicates that in these series, the effect of substituents is considerably greater in the carbon compounds. Further, a direct comparison in the same solvent between benzoyl chloride and diphenylphosphinyl chloride indicates that the latter undergoes ethanolysis some 23 times faster (at —8·5°). This factor is again similar to that obtained in the comparison of phosphorochloridates and chloroformates. It should be noted that as a consequence of the considerable difference in activation energies, the relative rates presented here depend somewhat upon the temperature at which the comparison is made.

TABLE 2. *Comparison of rates of solvolysis of phosphinyl chlorides with those of acetyl and benzoyl chlorides at —8·5°.*

	10^4k_1	E_A, kcal./mole
Acetyl chloride [a] ...	7·6	14·4
Benzoyl chloride [a] ...	0·075	12·5
Benzoyl chloride [b] ...	0·29	15·5
Dimethylphosphinyl chloride [c]	60·0	—
Diphenylphosphinyl chloride [c]	6·8	11·0

[a] Calc. from results of Branch and Hixon (*loc. cit.*) for 40% ethanol–60% ether as solvent. [b] Calc. from results of Morris (*loc. cit.*) for ethanol as solvent. [c] Calc. from authors' results (*J.*, 1953, 503).

The close analogy of the groupings $>$POCl and —COCl lends further support to the formulation using a double bond between the phosphorus and the oxygen atom and not to that using a " co-ordinate link " or " semipolar bond," still commonly employed. In these compounds the phosphorus atom utilizes a 3*d* orbital for its bonds, as it does in PCl_5, PBr_5 and the oxyhalides, and in agreement with the observed P–O bond lengths in the phosphate group and oxyhalides (cf. Pauling, " The Nature of the Chemical Bond," Cornell Univ. Press, 1944, pp. 84, 244).

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