101. *Kinetic Studies in the Phosphinyl Chloride and Phosphorochloridate Series.* Part I. Solvolytic Reactions.*

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A kinetic investigation of the solvolysis of five phosphorochloridates * and two phosphinyl chlorides in a wide range of solvents and at several temperatures is reported. The kinetic behaviour, and in particular the effects of variations in the structure, solvent, and added salts, indicate that a bimolecular mechanism operates in all these reactions.

Reactions of phosphorochloridates and phosphinyl chlorides have been studied kinetically in order to elucidate the mechanisms operating in reactions involving the phosphorus–halogen bond and to compare them with the reactions of analogous carbon compounds. Studies of solvolytic reactions are recorded in Part I, and Parts II and III deal with reactions with anionic nucleophilic reagents and with amines, respectively. The reactions are discussed in Part IV.

The compounds studied had the general formula Cl·PR$_2$O and included two phosphinyl chlorides (R = Me, Ph) and five phosphorochloridates (R = MeO, EtO, Pr^{i}O, CH$_2$Ph·O, PhO). Apart from some measurements on the analogous phosphorofluoridates (fluorophosphonates) (Mazur, *J. Biol. Chem.*, 1946, **164**, 271; Waters and de Worms, *J.*, 1949, 926; Kilpatrick and Kilpatrick, *J. Phys. Coll. Chem.*, 1949, **53**, 1371), no kinetic study of the reactions of this class of compound has been reported. The solvolytic reactions now investigated included those in dry methanol, dry ethanol, a number of aqueous-ethanolic media, water, deuterium oxide, and wet formic acid. The results for all the members of the series in dry ethanol and 80% ethanol are presented in Tables 1 and 2.

Table 1. *First-order rate constants* (10^4*k*, sec.$^{-1}$) *for the solvolysis of phosphorochloridates and phosphinyl chlorides in dry ethanol and in* 80% *aqueous ethanol.*

R	Temp.	100% EtOH	80% EtOH *	R	Temp.	100% EtOH	80% EtOH *
			Phosphorochloridates, Cl·PO(OR)$_2$.				
Me	39·6°	9·5 ± 0·6	76 ± 2	Et	39·6°	5·1 ± 0·4	—
	10·1	1·3 ± 0·3	9·5 ± 0·5		25·14	1·7 ± 0·2	13·7 ± 0·5
	0	0·56 ± 0·06	3·6 ± 0·5		10·1	0·5 ± 0·1	4·1 ± 0·3
	−12·9	0·19 ± 0·03	1·31		0	0·23 ± 0·01	1·8 ± 0·1
CH$_2$Ph ...	39·6	11 ± 1	64 ± 1	Pr^i	63·8	—	37·1 ± 0·5
	25·2	3·5 ± 0·3	—		39·6	1·78 ± 0·03	9·5 ± 0·5
Ph	39·6	8·5 ± 0·5	—		25·2	0·61 ± 0·02	3·0 ± 0·1
	25·2	3·2 ± 0·2	63 ± 1		10·1	0·19 ± 0·02	—
	−8·5	—	4 ± 1		0	0·097 ± 0·003	—
			Phosphinyl chlorides, Cl·PR$_2$O.				
Me	−8·5	60 ± 10	—	Ph	25·2	73 ± 7	—
					−0·2	13 ± 1	—

* 80% Ethanol is the solvent obtained by mixing 4 vols. of dry ethanol with 1 vol. of distilled water.

Table 2. *Arrhenius parameters for solvolyses of phosphorochloridates and phosphinyl chlorides in dry ethanol and in* 80% *aqueous ethanol.*

R in PR$_2$Cl:O	Solvent	*E* (kcal./mole)	10^{-6}*A* (sec.$^{-1}$)	R in PR$_2$Cl:O	Solvent	*E* (kcal./mole)	10^{-6}*A* (sec.$^{-1}$)
OMe	100% EtOH	12·0	0·25	OPr^i	100% EtOH	12·8	0·16
	80% ,,	12·5	4·2		80% ,,	12·9	0·87
OEt	100% ,,	13·4	1·2	OCH$_2$Ph	100% ,,	14·6	17
	80% ,,	13·5	11	OPh	100% ,,	11·9	0·18
Ph	100% ,,	11·4	1·7				

Since in solvolytic reactions the observed reaction order is not indicative of the mechanism, other considerations must be used to show the course of the reaction (cf. Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603; *Quart. Reviews*, 1951, **4**, 245). Although

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* The nomenclature used in this series of papers conforms with the recent American-British agreement, Sept. 1952 (cf. *Proc.*, 1952, 138).

we have not applied all the available methods for determining the mechanism rigorously, yet from those tests which were carried out, we think there is little doubt that the solvolyses are bimolecular in all the solvents tried. This conclusion is based on considerations detailed under the three headings which follow.

(a) *Effect of Added Nucleophilic Reagents.*—Both anionic (*e.g.*, hydroxide, ethoxide, and fluoride ions) and neutral nucleophilic reagents (*e.g.*, amines) have a powerful effect on the rates of reaction of the chlorides considered. These reactions are discussed fully in the following papers, but it may be stated here that the observed reaction rates of the solvolytic reactions are in keeping with the much weaker nucleophilic character of the solvents used than of the nucleophilic reagents mentioned above.

(b) *Effect of Solvent Variation.*—The data in Tables 1 and 2 show that all the halides react more rapidly in 80% than in 100% ethanol. Changes in the solvent seem to affect primarily the frequency factor, leading to a net increase in the rate of reaction in the aqueous media. A similar situation has been noted for a number of other reactions (cf. Hinshelwood, *Trans. Faraday Soc.*, 1938, **34**, 138). To examine the effect of changes in solvent further, the solvolysis of di*ïso*propyl phosphorochloridate was studied in a wider range of media. The results are summarised in Table 3 and the corresponding Arrhenius parameters are in Table 4.

TABLE 3. *Solvolysis of di*ïso*propyl phosphorochloridate in various solvents.* [First-order rate constants, k_1(sec.$^{-1}$) × 10^4.]

	Solvent									
Temp.	$H{\cdot}CO_2H$ *	100% MeOH	100% EtOH	95% EtOH	90% EtOH	80% EtOH	60% EtOH	10% EtOH	H_2O	D_2O
63·8°	—	—	—	—	—	37·1	84	—	—	—
39·60	0·06	—	1·78	—	5·53	9·5	—	—	—	—
25·14	0·008	2·44	0·61	1·41	2·03	3·0	5·8	—	81	65
10·08	—	—	0·19	—	0·65	—	—	—	—	—
0·0	—	—	0·97	—	—	—	0·63	8·6	8·6	—

* These values should be regarded as upper limits (see p. 504). No reaction could be detected in *tert.*-butyl alcohol after 7 days at 40°.

TABLE 4. *Arrhenius parameters for solvolysis of di*ïso*propyl phosphorochloridate in various solvents.*

	100% EtOH	90% EtOH	80% EtOH	60% EtOH	H_2O	$H{\cdot}CO_2H$
E (kcal./mole) ...	12·8	12·5	12·8	14·1	14·4	25·5
$A \times 10^{-6}$ (sec.$^{-1}$)...	0·16	0·3	0·8	14	290	4·0 × 10^6

Change of solvent from a less aqueous to a more aqueous medium accelerates the solvolytic reactions proceeding by both unimolecular and bimolecular mechanisms. However, the effects on the former are much greater than on the latter (Hughes, *Trans. Faraday Soc.*, 1941, **37**, 603; Dostrovsky and Hughes, *J.*, 1946, 167). The same facts were presented recently in a more quantitative manner by Winstein, Grunwald, and Jones (*J. Amer. Chem. Soc.*, 1951, **73**, 2700), who plot the logarithms of the rate constants against a function *Y*, which represents the ionising ability of the solvent, and obtain straight lines of different slope. Analysis of the data in Table 3 by either method leads to the conclusion that, in aqueous-ethanolic media, the effect of changes in water content on the rate of solvolysis corresponds to that expected from a bimolecular reaction; *e.g.*, a plot of the logarithms of the rate constants for ethanolic media against the corresponding *Y* values yields a straight line of slope 0·33, almost identical with that obtained in a similar plot for the solvolysis of ethyl bromide (0·34).

Of far greater significance is a comparison of the rates of solvolysis in formic acid and in an aqueous-ethanolic solvent of similar ionising capacity (Bateman and Hughes, *J.*, 1940, 941; Dostrovsky and Hughes, *J.*, 1946, 171; Winstein, Grunwald, and Jones, *loc. cit.*), for only in the case of a truly unimolecular solvolysis will the rate constants in the two media be similar. In solvolysis which is partly or wholly bimolecular, a change from the relatively strongly nucleophilic aqueous ethanol to the very weakly nucleophilic formic acid will lead to a great reduction in rate. For instance, methyl and ethyl bromides, which are typical of halides undergoing solvolysis by an essentially bimolecular process in aqueous ethanol, react some 200 and 80 times slower respectively in formic acid than in aqueous ethanol of equal ionising capacity (*ca.* 40% ethanol). On the other hand, for *tert.*-butyl chloride and *neo*pentyl bromide, the rates of solvolysis change little on passing from aqueous ethanol to formic acid. This has already been used in demonstrating the unimolecular nature of the solvolysis of *neo*pentyl bromide. The reaction of di*iso*propyl phosphorochloridate with formic acid differs from the other solvolyses in that the *iso*propoxy-groups are split off in addition to the chlorine atom (cf. p. 506). In fact, in view of the high values of the activation energy and frequency factor for this reaction (cf. Table 4), it is probable that the reaction measured is the acid-catalysed hydrolysis of the ester. The rate measured can therefore be regarded as an upper limit for the rate of removal of the chlorine atom, and can be safely used for the comparison which follows. Thus, it is seen that the rate of solvolysis of di*iso*propyl phosphorochloridate decreases greatly on passing from aqueous ethanol to formic acid, a fact supporting the bimolecular mechanisms of this reaction. These arguments are summarised in Table 5.

TABLE 5. *Relative rates for solvolysis of some halides in " 40% " aqueous ethanol and in wet formic acid.*

Halides :	MeBr	EtBr	Bu^tCl	$CMe_3{\cdot}CH_2Br$	$Cl{\cdot}PO(OPr^i)_2$
k(40% EtOH)/k($H{\cdot}CO_2H$)	200 [a]	80 [a]	0·89 [b]	1·61 [c]	2000 [d]

[a] Winstein, Grunwald, and Jones (*loc. cit.*). [b] Calculated from results of Hughes (*J.*, 1935, 255) and of Bateman and Hughes (*J.*, 1937, 1187). [c] Calc. from results of Dostrovsky and Hughes (*J.*, 1946, 166, 171). [d] Lower limit, calc. from data of Table 3.

(c) *Effect of Acids, Salts, and Silver Ions.*—The absence of any marked drift in the rate constant of the solvolysis reaction with the course of reaction indicates the absence of acid catalysis (for the medium becomes acid during reaction) and the absence of a strong ionic effect. As a further check, the reactions were specifically tested for acid and salt effects by carrying out solvolyses with the initial addition of sulphuric acid and various salts. The results are listed in Table 6.

TABLE 6. *Solvolysis of di*iso*propyl phosphorochloridate in the presence of various reagents.*

Temp.	EtOH, %	Phosphorochloridate concn.	Additional component	1st-order rate constant 10^4k_1 (sec.$^{-1}$)
25·15°	100	0·09	None	0·61
25·15	100	0·08	0·10N-H_2SO_4	0·63
0	10	0·04	None	8·6
0	10	0·036	0·13N-H_2SO_4	8·3
25·15	60	0·05	None	5·7
25·15	60	0·06	0·1N-KNO_3	6·2
25·15	60	0·05	0·11N-$AgNO_3$	9·0
25·15	100	0·07	0·2N-$NaClO_4$	0·9
25·15	100	0·06	0·2N-NH_4NO_3	0·9

It has been shown on the basis of arguments similar to those used in analysing solvent effects on solvolytic reactions (Bateman, Church, Hughes, Ingold, and Taher, *J.*, 1940, 979) that addition of salts to the solvolysis medium increases both the unimolecular and the bimolecular rates of reaction and that the effect is expected to decrease in going to more aqueous solvents. Examination of the data of Table 6 shows that, as expected for a reaction between neutral molecules, a positive salt effect operates, and that it is less in the more aqueous solvent. The limited precision of the data and the lack of reference experiments precluded the use of these salt effects to differentiate between the two possible mechanisms of reaction.

The absence of acid catalysis should be particularly noted, for in the solvolysis of the phosphorofluoridates, marked acid catalysis has been observed (Waters and de Worms; Kilpatrick and Kilpatrick; *locc. cit.*). The small effect of silver ions shows the resistance of the phosphorus–halogen bond to electrophilic attack, which also is a measure of its reluctance to undergo reaction by an ionisation mechanism (cf. Dostrovsky and Hughes, *J.*, 1946, 169). That the course of reaction is indeed represented by the equation $PR_2OCl + R'OH = PR_2O(OR') + HCl$, where R = alkyl or alkoxy and R' = H or alkyl, has been shown by examination of reaction products. Esters of phosphoric acid and of phosphinic acids have been obtained from reactions with dry alcohols. From reactions in highly aqueous solvents (*e.g.*, 10% ethanol) the free acids $PR_2O{\cdot}OH$ were isolated. On the other hand, in reactions in less aqueous ethanolic media, mixtures of ester and free acid are formed, as shown by analysing the reaction mixture for chloride and hydrogen ions. Since free dialkyl hydrogen phosphates are strong acids, the excess of hydrogen ions over the chloride ions is a measure of the proportions of the reaction of the phosphorochloridate with water molecules. In this way it has been shown that in the solvolysis of di*iso*propyl phosphorochloridate in 80% aqueous ethanol the ratio of ethyl di*iso*propyl phosphate to di*iso*propyl hydrogen phosphate is 1·22. Since in this solvent the concentrations of ethanol and water are about the same (in moles/l.) this is also the ratio of the nucleophilic power of ethanol to that of water in the relevant reaction.

EXPERIMENTAL

M. p.s are uncorrected.

Materials.—*Dialkyl phosphorochloridates.* The methyl, ethyl, and *iso*propyl esters were prepared from the corresponding dialkyl hydrogen phosphites by chlorination in carbon tetrachloride (McCombie, Saunders, and Stacey, *J.*, 1945, 380) and purified by vacuum-distillation: dimethyl ester, b. p. 80—83°/23 mm. (Found: Cl, 23·5. Calc. for $C_2H_6O_3ClP$: Cl, 24·6%); diethyl ester, b. p. 28—30°/0·5 mm. (Found: Cl, 20·8. Calc. for $C_4H_{10}O_3ClP$: Cl, 20·5%); di*iso*propyl ester, b. p. 43—47°/0·5 mm. (Found: Cl, 18·0. Calc. for $C_6H_{14}O_3ClP$: Cl, 17·8%).

Dibenzyl phosphorochloridate was prepared by Sheehan and Frank's modification (*J. Amer. Chem. Soc.*, 1950, **72**, 1314) of Atherton, Openshaw, and Todd's method (*J.*, 1945, 382), and the oil finally obtained was used for the kinetic experiments without further purification. The diphenyl ester, prepared according to Brigl and Muller (*Ber.*, 1939, **72**, 2121), had b. p. 140—155°/1 mm. (Found: Cl, 13·3. Calc. for $C_{12}H_{10}O_3ClP$: Cl, 12·5%).

Dimethylphosphinyl chloride was prepared according to Kabachnik and Shepeleva (*Izvest. Akad. Nauk, U.S.S.R.*, Otdel. Khim. Nauk, 1949, **1**, 56; see also Kosolapoff and Watson, *J. Amer. Chem. Soc.*, 1951, **73**, 5466). The chloride sublimed at 0·5 mm., at an oil-bath temperature of about 150°, and condensed in the receiver as colourless crystals, m. p. 68—69° (Found: Cl, 32·2. Calc. for C_2H_6OClP: Cl, 31·5%).

NN-*Diëthylphosphoramidic dichloride*, $NEt_2 \cdot POCl_2$. To diethylamine (103 ml., 1 mole) in carbon tetrachloride (300 ml.) in a 3-necked flask cooled in brine, phosphorus oxychloride (46 ml., 0·5 mole) was added dropwise with stirring, under protection of a calcium chloride guard-tube. After several hours the solvent was evaporated, and the residual semi-solid distilled under reduced pressure, yielding 69 g. (73%) of a colourless oil, b. p. 129—133°/37 mm. (Found: Cl, 34·2. Calc. for $C_4H_{10}ONCl_2P$: Cl, 35·4%). Michaelis (*Annalen*, 1903, **326**, 129) gave b. p. 100°/15 mm. The product was used without further purification for the following reaction.

Diphenylphosphinyl chloride was prepared by Kosolapoff's modification (*J. Amer. Chem. Soc.*, 1949, **71**, 369) of Michaelis and Wegner's method (*Ber.*, 1915, **48**, 316) for the synthesis of arylphosphinic acids. The acid had m. p. 187°. Michaelis and Wegner (*loc. cit.*) gave m. p. 190°. The chloride had b. p. 165—160°/1 mm. (Found: Cl, 14·6. Calc. for $C_{12}H_{10}OClP$: Cl, 15·0%). The oil is very hygroscopic and is hydrolysed by atmospheric moisture to the acid.

Solvents for Rate Measurements.—Methanol was distilled from magnesium methoxide (Lund and Bjerrum, *Ber.*, 1931, **64**, 210). Ethanol was distilled from calcium oxide and then from sodium and ethyl phthalate (Manske, *J. Amer. Chem. Soc.*, 1931, **53**, 1106); some samples of it were shown, by titration with Karl Fischer's reagent (Mitchell and Smith, "Aquametry," Interscience Publ., 1948), to contain less than 0·01% of water. *tert.*-Butyl alcohol was refluxed with sodium and distilled. Formic acid, 98—100% (Baker and Adamson, C.P.), was recrystallised four times; its m. p. was 7·1°, so it contained 0·5—1% of water.

Phosphate esters. The phosphorochloridate, $(RO)_2POCl$, was refluxed with 10 vols. of absolute ethanol for $\frac{1}{2}$ hour, then cooled; barium carbonate was added in slight excess, and the excess filtered off. The ethanol was evaporated off under reduced pressure, and the residue fractionated, yielding odourless oils. Ethyl dimethyl phosphate had b. p. 112—113°/41 mm. (Found: C, 31·2; H, 7·6. Calc. for $C_4H_{11}O_4P$: C, 31·2; H, 7·2%), n_D^{22} 1·3984, the triethyl ester, b. p. 211°/754 mm., n_D^{20} 1·4051, and the *ethyl di*iso*propyl* ester, b. p. 110—112°/25 mm. (Found: C, 46·2; H, 9·2; P, 14·5. $C_8H_{19}O_4P$ requires C, 45·7; H, 9·1; P, 14·8%), d_{25}^{25} 1·0066, n_D^{25} 1·4044. Ethyl diphenyl phosphate had b. p. 181—185°/2 mm. (Found: C, 61·4; H, 5·9; P, 10·6. Calc. for $C_{14}H_{15}O_4P$: C, 60·4; H, 5·4; P, 11·2%), d_{25}^{25} 1·185, n_D^{30} 1·5250 (Morel, *Bull. Soc. chim.*, 1899, **21**, 492, gives b. p. 211—221°/18 mm., d_0^0 1·2113).

*Di*iso*propyl hydrogen phosphate.* Di*iso*propyl phosphorochloridate (4·0 g.) was mixed with water and ethanol (9 : 1), and the solvents evaporated at 50° under reduced pressure, first with a water-pump and finally for several hours with a high-vacuum system. The residual colourless oil, crystallised by freezing with liquid air, formed white crystals, m. p. 34° (3·3 g.) (Found: C, 39·6; H, 8·3; P, 17·0%; equiv., by potentiometric titration with NaOH and a glass electrode, 184. $C_6H_{15}O_4P$ requires C, 39·6; H, 8·2; P, 17·5%; equiv., 182). *Di*iso*propyl hydrogen phosphate* has not been recorded but its lead salt was prepared by Cavalier and Pros (*Bull. Soc. chim.*, 1900, **23**, 679). The guanidine salt, m. p. 156—157°, was prepared from guanidine carbonate (Wagner-Jauregg, O'Neil, and Summerson, *J. Amer. Chem. Soc.*, 1951, **73**, 5205) and precipitated by acetone.

Products of Solvolysis of Phosphorochloridates in "80%" Ethanol.—A solution of the di*iso*propyl ester (0·2336 g.) in 80% ethanol (10 ml.) was kept for 21 hours at about 25° and then required 18·50 ml. of 0·100N-NaOH (methyl-red) and 11·27 ml. of 0·100N-$AgNO_3$ (Calc.: 11·65 ml.). The excess of acidity over chloride, 18·50 − 11·27 = 7·23 ml., is equivalent to the amount of di*iso*propyl hydrogen phosphate formed. The proportion of the total reaction due to hydrolysis is thus 7·23 × 100/11·27 = 64%.

*Solvolysis of Di*iso*propyl Phosphorochloridate in Formic Acid.*—This ester (0·4963 g.) in 98% formic acid (10 ml.) in a glass-stoppered flask was kept for 6 days at 40° in a thermostat. The solvent was then evaporated off at room temp./2 mm. during 4 hours. A viscous liquid dibasic acid remained (0·2747 g.) [Found: P (as $Mg_2P_2O_7$), 31·2%; equiv., by titration with NaOH (methyl-red), 102; (phenolphthalein), 52. Calc. for H_3PO_4: P, 31·6%; equivs., 98, 49]. It gave the molybdate test for orthophosphoric acid, and in ammonia solution, gave magnesium ammonium phosphate (alkyl phosphates do not give a precipitate under these conditions; Bailly, *Bull. Soc. chim.*, 1919, **25**, 255). Thus in formic acid solution, di*iso*propyl phosphorochloridate was quantitatively decomposed into orthophosphoric acid. Since it is not certain whether the cleavage of the alkyl group preceded or succeeded the removal of the chlorine, the rate constants for this reaction presented in this paper must be regarded as upper limits only.

Kinetic Measurements.—All kinetic runs were made in thermostats controlled to better than 0·03°; those above room temperature contained water with an upper layer of paraffin, those below room temperature contained an aqueous solution of ethylene glycol and were placed in another cooled thermostat controlled to within 0·5°. The temperature of the thermostats of −8·5° and −12·9° was measured with a chromel–alumel thermocouple calibrated at the m. p. of redistilled mercury. Three methods were used for following the solvolysis: titration of the liberated chloride, titration of the liberated acid, and conductometric measurement of liberated ions.

Titration of liberated chloride. A weighed amount of the phosphorochloridate in a 25- or 30-ml. flask was placed in the thermostat, and the volume adjusted with the required solvent at the thermostat temperature. Samples of 3 or 5 ml. were stirred into 20—25 ml. of 95% ethanol which had been chilled to −20°. A stop-watch was started when the liquid of the first sample had passed a definite mark on the pipette.

The chloride-ion concentration was determined by a modification of Cavanagh's method (*J.*, 1927, 2207) with an electrode of silver wire covered by a thin layer of electrodeposited silver chloride. The reference electrode consisted of a glass tube 8 mm. in diameter, in the bottom of which was a ground-glass stopper which assured liquid contact between the contents of the tube and the solution of chloride surrounding it. The reference electrode tube contained a platinum electrode and was filled with a phosphate–citrate buffer of pH 3·2 containing some quinhydrone. As shown by Cavanagh, the P.D. between a quinhydrone electrode at pH 3·2 and a silver chloride electrode immersed in a saturated solution of silver chloride (containing equivalent amounts of Ag^+ and Cl^-) is zero. Thus at the end-point of the titration of a chloride solution with silver nitrate the potential between the electrodes vanished. The potential difference was measured with a Model H, Beckman glass-electrode pH meter. The silver electrode was connected to the terminal which was usually connected to the calomel electrode, and the platinum electrode was connected through a 160-megohm resistor in series to the other terminal. This procedure was adequate for estimating the chloride liberated from di*iso*propyl phosphorochloridate, for during the period of titration (1—2 minutes) the extent of solvolysis of this ester is very small. However, with the other phosphorus chlorides tested the rate of solvolysis is larger and the results are erratic.

Titration of liberated acid. Since tertiary amines at room temperature react very slowly with dialkyl phosphorochloridates (see Part III, *J.*, 1953, 511), a solution of triethylamine in acetone was used to titrate the acid liberated in the solvolysis. Lacmoid was used as an indicator, giving a very brilliant colour change. This method was used mainly for following the ethanolysis of the dimethyl ester (cf. also Böhme, *Ber.*, 1941, **74**, 246).

Conductivity method. Smooth platinum electrodes were sealed in the sides of 8—30-ml. Pyrex-glass volumetric flasks and connected with side-limbs containing mercury. Solvent was added to a level about 1 cm. above the electrodes, and the cell thus formed closed with a ground-glass stopper and immersed for ½ hour in the thermostat. A small drop of the chloride was added from a capillary and dissolved by shaking. At measured times the conductivity was determined with a bridge assembly of the type described by Jones and Josephs (*J. Amer. Chem. Soc.*, 1928, **50**, 1049) with a 1300-cycles phase-shift audio-oscillator (Kunde, " Electronics Manual for Radio Engineers," McGraw Hill, 1949, p. 121). The bridge permitted measurement from 99,000 to 0·1 ohm. The output of the bridge was amplified through a peaked audio-amplifier (" Radio Amateur's Handbook," 1949, p. 127; American Radio Relay League) and detected with head-phones. Conductivity was measured by balancing condensers and resistors, giving an accuracy of at least 0·1%.

At first, the relation between conductivity and concentration of solvolysis products was determined in special measurements, and it was found that at the high dilutions used (0·001—0·01M) conductivity was, within the limits of accuracy, proportional to concentration. It was thus possible to calculate the first-order rate constants directly from the measurements of each run without introducing the further errors of an empirical calibration curve. This method gave satisfactory results for the solvolysis of phosphorus chlorides in aqueous solvents; in absolute ethanol the rate constants were less reproducible and deviations of up to ±10% were encountered. As shown by Norris, Fasce, and Staud (*J. Amer. Chem. Soc.*, 1935, **57**, 1416), the conductivity of hydrogen chloride in absolute ethanol is affected by traces of moisture and other impurities; precise results were obtained only with very elaborate precautions.

The main advantage of the conductivity method is the possibility of measurement of rates of reactions with half-lives as short as 1 minute, and use of only very small amounts of material.

Typical Determinations of First-order Rate Constants (k_1) *of Solvolysis.*—(a) *Hydrolysis of di*iso*propyl phosphorochloridate* (*initial concn.* 0·00073M) *in water at* 25·14°. (Conductivity method.) First-order rate constants $k_1 = (2·3/t) \log (\kappa_\infty - \kappa_0)/(\kappa_\infty - \kappa_t)$, where κ_0, κ_t, and κ_∞ are the reciprocals of resistance at time zero, t, and infinity, respectively.

Time, min. ...	0	0·25	0·5	0·75	1·0	1·25	1·5	1·75	2·25	2·75	∞
Ohms	1440	1310	1210	1140	1080	1030	990	950	900	870	757
10^4k_1 (sec.$^{-1}$)	—	78·0	78·4	77·1	77·3	77·8	78·1	80·8	81·2	78·6	—

Mean $k_1 = 79·5 \times 10^{-4}$ sec.$^{-1}$.

(b) *Solvolysis of di*iso*propyl phosphorochloridate in* 80% *ethanol at* 25·14°. (Conductivity method.)

Time, min.	0	9	19	28	38	45	53	61	∞
Ohms	21,500	10,600	7300	5910	4980	4600	4200	3960	2761
10^4k_1 (sec.$^{-1}$)	—	3·00	2·96	2·93	2·96	2·88	2·94	2·91	—

Mean $k_1 = 2·96 \times 10^{-4}$ sec.$^{-1}$.

(c) *Solvolysis of di*iso*propyl phosphorochloridate* (*initial concn.* 0·044M) *in* 80% *ethanol at* 25·14°. [Titration of chloride method: $k_1 = (2·3/t) \log (x_\infty - x_0)/(x_\infty - x)$].

Time, sec.	0	158	392	564	746	975	1466	2210	3992	∞
0·00984N-$AgNO_3$, ml.	2·04	3·03	4·50	5·39	6·46	7·60	9·66	12·37	16·61	22·88
10^4k_1 (sec.$^{-1}$)	—	3·07	3·19	3·11	3·19	3·18	3·10	3·09	3·01	—

Mean $k_1 = 3·12 \times 10^{-4}$ sec.$^{-1}$.

(d) *Solvolysis of di*iso*propyl phosphorochloridate* (0·088M) *in absolute ethanol at* 25·14°. (Titration of chloride method.)

Time, sec.	0	390	715	1300	1761	3067	5439	∞
0·00984N-$AgNO_3$, ml.	3·31	4·40	5·13	6·60	7·79	10·70	15·84	45·70
10^4k_1 (sec.$^{-1}$)	—	0·66	0·61	0·62	0·63	0·62	0·64	—

Mean $k_1 = 0·62 \times 10^{-4}$ sec.$^{-1}$.

(e) *Solvolysis of diphenylphosphinyl chloride* (0·0016M) *in absolute ethanol at* 25·14°. (Conductivity method.)

Time, min.	0	1·0	1·5	2·0	3·0	4·0
Ohms	13,000	84,000	7500	6900	6210	5810
10^4k_1 (sec.$^{-1}$)	—	74·0	74·1	72·6	70·3	69·6

Mean $k_1 = 72 \times 10^{-4}$ sec.$^{-1}$.

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[*Received, September* 1*st*, 1952.]