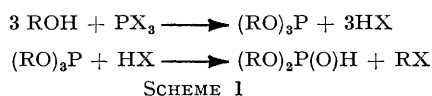


Quasiphosphonium Intermediates. Part II.¹ Protonation of Trialkyl Phosphites and the Mechanism of their Dealkylation by Hydrogen Chloride

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Variable temperature ³¹P n.m.r. studies of solutions of trineopentyl phosphite and hydrogen chloride in dioxan and ether show that rapidly reversible protonation occurs at room temperature. At -40° or below, the site of protonation is identified as the phosphorus atom [δ -24.9 p.p.m. from 85% H₃PO₄ (J_{PH} 834 ± 6 Hz)]. Although dealkylation of less sterically hindered phosphites occurs rapidly above -50°, the protonated form of tri-n-butyl phosphite can be obtained at -70°. Reversible formation of dialkyl phosphorochloridite, which appears to require initial protonation at oxygen, also takes place to a small extent. The kinetics of the first dealkylation of the trialkyl phosphites (RO)₃P (R = Me, Et, Prⁿ, or Buⁿ) by hydrogen chloride in dioxan have been measured at 25°. For tri-n-butyl phosphite the dealkylation was shown to be first order in phosphite and second order in hydrogen chloride, if the former is in excess ($\geq 10:1$ molar). The results are consistent with rapid reversible protonation of the phosphite, followed by slow nucleophilic displacement of the alkyl group by either the hydrogen dichloride anion or a second molecule of hydrogen chloride. With more nearly equal concentrations of reactants it is not possible to distinguish between processes which are second and third order in hydrogen chloride. Variations in the observed overall third-order rate constant with changing reactant ratios might be due to changes in the order in hydrogen chloride.

THE dealkylation of trialkyl phosphites by hydrogen halides constitutes the principal route to alkyl halide formation in alcohol-phosphorus trihalide interactions. The latter also afford the best method for the preparation of dialkyl phosphonates (Scheme 1).²



Information has been obtained concerning the mechanism of *O*-alkyl fission by studies of optical activity and alkyl rearrangement, the results being indicative of an S_N2 mechanism in the case of unhindered straight chain primary or secondary alkyl groups,³ and of concurrent S_N1 and S_N2 mechanisms in the case of more hindered alkyl groups such as neopentyl⁴ or 1,2-dimethylpropyl.⁵

Qualitative rate studies on the dealkylation of a variety of trialkyl phosphites, dialkyl phosphonates, and trialkyl phosphates have previously been made,^{6,7} and it has been shown⁶ that the rates for the successive removal of alkyl groups from tri-n-butyl phosphite are in the order first \gg second $>$ third. On the assumption that consecutive second-order reactions are involved in the removal of the two ethyl groups of diethyl hydrogen phosphite by hydrogen bromide in diethyl ether, the relative rates for these two dealkylation steps were shown to be *ca.* 9 : 1.⁸ The dealkylation of di-isopropyl hydrogen phosphite by hydrogen chloride in the absence of solvent has also been studied and was found to obey

second-order kinetics with respect to hydrogen chloride.⁹ These results were interpreted in terms of nucleophilic attack on a phosphite-hydrogen chloride complex by a second molecule of hydrogen chloride.

It was the purpose of the present work to investigate the reaction between hydrogen chloride and a number of trialkyl phosphites under conditions which enabled only the first dealkylation to be observed.

RESULTS AND DISCUSSION

Our first experiments were made in order to investigate the initial interaction of the phosphite with hydrogen chloride and to identify, if possible, any intermediate which might be formed. Trineopentyl phosphite was used for this purpose since its rate of dealkylation by hydrogen chloride is immeasurably slow. Its use has also made possible the isolation of an intermediate in the related Michaelis-Arbuzov reaction.^{1,10}

At 25°, in either ether or dioxan, the ³¹P n.m.r. spectrum showed a sharp singlet whose chemical shift varied, according to the relative and absolute concentrations of reactants (Table I), between that of the pure phosphite (δ -139.8 p.p.m.) and a value (*ca.* -20 p.p.m.) associated with the protonated species (see below). Coupling between phosphorus and the methylene protons also disappeared. Rapid exchange between the phosphite and one or more hydrogen-bonded and/or protonated species is indicated. On

¹ Part I, H. R. Hudson, R. G. Rees, and J. E. Weekes, *J.C.S. Perkin I*, 1974, 982.

² W. Gerrard and H. R. Hudson, 'Organic Derivatives of Phosphorous Acid and Thiophosphorous Acid,' ch. 13, pp. 23, 54 in 'Organic Phosphorus Compounds,' eds. G. M. Kosolopoff and L. Maier, Wiley, New York, 1973, vol. 5.

³ T. M. Cook, E. J. Coulson, W. Gerrard, and H. R. Hudson, *Chem. and Ind.*, 1962, 1506; E. J. Coulson, W. Gerrard, and H. R. Hudson, *J. Chem. Soc.*, 1965, 2364; D. G. Goodwin and H. R. Hudson, *J. Chem. Soc. (B)*, 1968, 1333; B. A. Chaudri, D. G. Goodwin, and H. R. Hudson, *ibid.*, 1970, 1290.

⁴ H. R. Hudson, *J. Chem. Soc. (B)*, 1968, 664.

⁵ R. A. Arain and M. K. Hargreaves, *J. Chem. Soc. (C)*, 1970, 67; B. A. Chaudri and H. R. Hudson, unpublished work.

⁶ W. Gerrard and E. G. C. Whitbread, *J. Chem. Soc.*, 1952, 914, and papers cited therein.

⁷ V. F. Cooke, W. Gerrard, and W. J. Green, *Chem. and Ind.*, 1953, 351; W. Gerrard, W. J. Green, and R. A. Nutkins, *J. Chem. Soc.*, 1952, 4076.

⁸ V. F. G. Cooke and W. Gerrard, *J. Chem. Soc.*, 1955, 1978.

⁹ C. H. Campbell and D. H. Chadwick, *J. Amer. Chem. Soc.*, 1955, 77, 3379.

¹⁰ H. R. Hudson, R. G. Rees, and J. E. Weekes, *Chem. Comm.*, 1971, 1279.

lowering the temperature of an approximately equimolar solution of trineopentyl phosphite and hydrogen chloride in diethyl ether (Table 2) the peak at -139.5

TABLE 1

^{31}P N.m.r. chemical shifts for trineopentyl phosphite-hydrogen chloride mixtures in dioxan at 25°

(RO) $_3$ P (mol %) ^a	HCl (mol %) ^a	Molar ratio HCl : (RO) $_3$ P	δ (p.p.m.) ^b
11.4	11.7	1.0	-108.8
13.7	20.6	1.5	-69.5
10.3	20.7	2.0	-57.7
9.9	23.2	2.3	-39.0
1.8	5.4	3.0	-115.2
3.7	11.2	3.0	-66.5
7.3	22.1	3.0	-31.2
7.1	44.9	6.3	-20.3

^a Percentage of total moles present (phosphite + HCl + dioxan). ^b Sharp singlets.

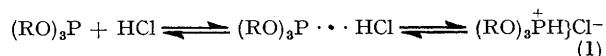
TABLE 2

Variable temperature ^{31}P n.m.r. data for trineopentyl phosphite-hydrogen chloride solutions in diethyl ether

(RO) $_3$ P (mol %) ^a	HCl (mol %) ^a	Molar ratio HCl : (RO) $_3$ P	Temp. ($^\circ\text{C}$)	δ (p.p.m.)
4.8	4.5	0.94	+25	-139.5 (s) ^b
			0	-134.0 (s)
			-30	-115.5br (s)
			-60	-139.0br (s); -33.0br (d, J_{PH} ca. 860 Hz)
3.4	22.3	6.6	+25	-36.8 (s) ^c
			0	-27.9 (s)
			-40	-25.7br (d, J_{PH} ca. 690 Hz)
			-50	-24.9 (d, J_{PH} 834 Hz)
			-70	-24.9 (d, J_{PH} 834 Hz) ^d

^a Percentage of total moles present (phosphite + HCl + ether). ^b (RO) $_2$ PCl (ca. 4%) also detected (δ -167.3 p.p.m.), decreasing to ca. 2% at -10° . ^c (RO) $_2$ PCl (ca. 10%) present, decreasing to ca. 3% (0°) and to ca. 1.5% at -40° and below. ^d Increased sharpness; otherwise no change from spectrum at -50° . Broad band proton decoupling at -60° caused collapse to a singlet.

p.p.m. gradually broadened and was resolved at -60° into a broad doublet [δ -33.0 p.p.m. (J_{PH} ca. 860 Hz)], assigned to the protonated species, and a signal due to free phosphite (-139.0 p.p.m.). With a large excess of hydrogen chloride (6.6:1 molar ratio) the original singlet occurred at -36.8 p.p.m. and was resolved at -50° into a sharp doublet centred at -24.9 p.p.m. (J_{PH} 834 Hz). Broad band proton decoupling caused the latter to collapse to a singlet. The magnitude of the coupling constant indicates the presence of a quasi-phosphonium species, protonated on phosphorus,^{11,12} but whether this is associated with the chloride ion only (1), or with the hydrogen dichloride ion (see below) is



SCHEME 2

uncertain. The averaged signal observed above -40° was seen to shift upfield as the temperature was lowered. This is consistent with a shift in equilibrium towards the protonated form and was accompanied by a correspond-

ing decrease in the amount of dineopentyl phosphorochloridite detectable in the system (see below).

We have confirmed the chemical shift for protonated trineopentyl phosphite by reaction of the latter with trifluoromethanesulphonic acid, which gave a low melting solid [δ (CDCl $_3$) -23.6 p.p.m. (J_{PH} 834 Hz)], thought to be [(Me $_3$ CCH $_2$ O) $_3$ PH] $^+$ SO $_3$ CF $_3$ $^-$. Purification was not possible as dealkylation occurred slowly at room temperature. Identification of the protonated forms of the tri-, di-, and mono-alkyl phosphite was achieved in the presence of an excess of CF $_3$ SO $_3$ H, when long-range coupling between phosphorus and the methylene protons gave rise to doublets of septets, quintets, and triplets, from the protonated tri-, di-, and mono-neopentyl esters respectively (Table 3).

TABLE 3

^{31}P N.m.r. data^a for protonated tri-, di-, and mono-neopentyl phosphite in CF $_3$ SO $_3$ H at 25°

(RO) $_3$ P (mmol)	CF $_3$ SO $_3$ H (mmol)	(RO) $_3\overset{\oplus}{\text{P}}\text{H}$		(RO) $_2\overset{\oplus}{\text{P}}(\text{OH})\text{H}$		RO $\overset{\oplus}{\text{P}}(\text{OH})\text{H}$	
		δ (p.p.m.)	J_{PH} (Hz)	δ (p.p.m.)	J_{PH} (Hz)	δ (p.p.m.)	J_{PH} (Hz)
7.2	7.3	-23.6 ^b	834 ^b	-11.5 ^b	744 ^b		
1.7	5.7	-22.0	816	-14.3	768		
c	11.4	-20.5	804	-17.7	798		
	22.8	-20.0	804	-18.0	810		
1.7	11.4	-21.1 ^d	810	-16.6 ^e	792	-15.4 ^f	786

^a CDCl $_3$ (10%) Used as internal lock. ^b Data for initial solid product, taken up in CDCl $_3$. ^c Cumulative totals for successive additions of CF $_3$ SO $_3$ H to same phosphite sample. ^d Doublet of septets, J_{POCH_2} 6.1 Hz. ^e Doublet of quintets, J_{POCH_2} 6.2 Hz. ^f Doublet of triplets, J_{POCH_2} 6.2 Hz.

It was also observed that with increasing acid concentration the chemical shift of the protonated trialkyl ester moved upfield from ca. -24 to -20 p.p.m. and that the P-H coupling constant decreased (834 to 804 Hz). In contrast, the chemical shift for protonated dineopentyl phosphite moved downfield and the P-H coupling constant increased, with increasing acid concentration. Similar results were observed for di-n-propyl phosphite which gave limiting values of δ -18 p.p.m. and J_{PH} 804 Hz in an excess of CF $_3$ SO $_3$ H (Table 4).

TABLE 4

^{31}P N.m.r. data for di-n-propyl phosphite (2.0 mmol) in CF $_3$ SO $_3$ H at 25°

CF $_3$ SO $_3$ H added (mmol) ^a	δ (p.p.m.) ^b	J_{PH} (Hz)
0	-7.0	691
3.4	-8.6	709
5.7	-13.1	762
9.3	-15.9	780
17.1	-16.9	798
Large excess	-17.6	804

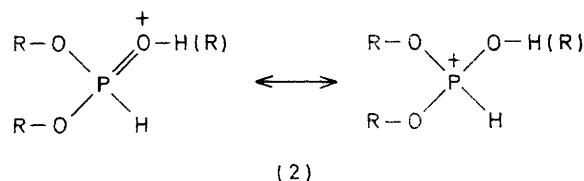
^a Cumulative totals for successive additions of CF $_3$ SO $_3$ H to same phosphite sample. ^b CDCl $_3$ (5%) Added as internal lock.

Variations in chemical shift and coupling constant for solutions of dimethyl hydrogen phosphite in carboxylic acids have been found to follow similar although less pronounced trends and have been interpreted in terms

¹¹ W. McFarlane and R. F. M. White, *Chem. Comm.*, 1969, 744.

¹² G. A. Olah and C. W. McFarland, *J. Org. Chem.*, 1971, **36**, 1374.

of varying association of the acidic proton with the phosphoryl oxygen.¹³ The present results suggest that both the di- and tri-esters become fully protonated under these strongly acidic conditions and that the structures of the protonated forms of each are similar (2).

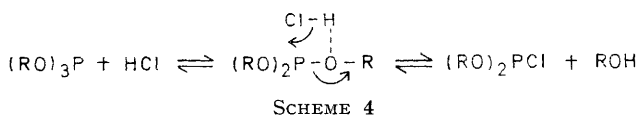


In 100% sulphuric acid at 25°, trineopentyl phosphite also gave a mixture of the various protonated forms and we consider, from the ease of dealkylation, that it is unlikely that protonated tri-methyl, -ethyl, and -isopropyl phosphites are the sole species to exist under these conditions¹¹ for more than a short time. Protonated phosphites have also been studied in $\text{SbF}_5\text{-FSO}_3\text{H}$ although in this medium dealkylation was rapid above -60° .¹² The protonated forms of tri-, di-, and mono-isopropyl phosphite were nevertheless observed at -60° although the chemical shifts reported were in the reverse order to those which we obtained for tri-, di-, and mono-neopentyl phosphite respectively in $\text{CF}_3\text{SO}_3\text{H}$ (Table 2).

Trialkyl phosphites other than the neopentyl ester are dealkylated too rapidly by HCl for the protonated form to be detectable at room temperature. However by mixing solutions of tri-*n*-butyl phosphite and hydrogen chloride in ether at -70° the protonated species was obtained. Dealkylation occurred fairly quickly at -50° . The rate of dealkylation at reduced temperatures is of significance in the manufacture of trialkyl phosphites, it being claimed¹⁴ that dealkylation at -20° is sufficiently slow for ROH-PCl_2 mixing to be possible at that temperature before ammonia gas is added to remove the hydrogen chloride by-product. Previous results indicate that the success of this procedure is more likely to be due to the fact that the final alkoxylation of phosphorus at -20° is slow (Scheme 3), especially in the presence of HCl produced in the earlier stages.¹⁵ Our present results demonstrate the reversi-



bility of this reaction, by the formation of small amounts of dineopentyl phosphochlorodite (δ -165 p.p.m.) in the trineopentyl phosphite-hydrogen chloride mixture. This reaction appears to require the involvement of an *O*-protonated phosphite (Scheme 4). In this connection



it is of interest to note that triphenyl phosphite, in which electron density at phosphorus is considerably reduced

¹³ W. J. Stec, J. R. Van Wazer, and N. Goddard, *J.C.S. Perkin II*, 1972, 463.

by mesomeric interaction of the oxygen lone pair with the phenyl group, gives no detectable amount of the *P*-protonated ester with HCl, but only diphenyl phosphorochloridite (Table 5).

TABLE 5
Reaction of triphenyl phosphite with hydrogen chloride

10^2 Initial [(PhO) ₃ P] (M)	10^2 Initial [HCl] (M)	K_e (33.5°) ^a
1.16	0.295	1.99
1.30	0.695	2.34
1.22	0.118	1.94

^a For the equilibrium $(\text{PhO})_3\text{P} + \text{HCl} \rightleftharpoons (\text{PhO})_2\text{PCl} + \text{PhOH}$.

The kinetics of dealkylation for a series of tri(primary alkyl) phosphites in dioxan were followed titrimetrically at 25°. Olefin formation, which would invalidate this

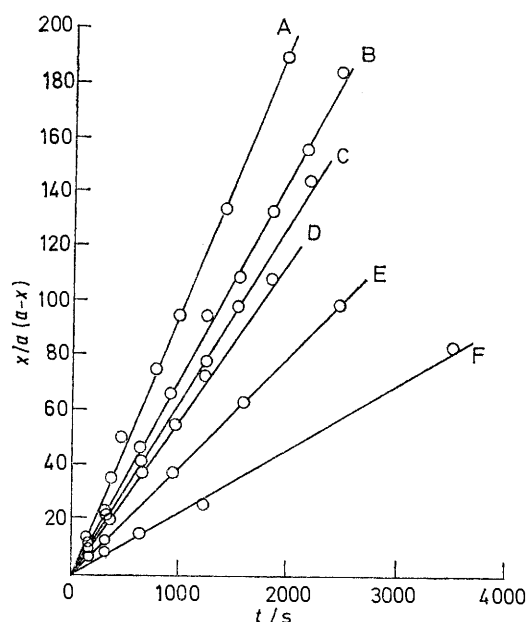


FIGURE 1 Plots of pseudo-second-order rate data for the interaction of various excesses of $(\text{BuO})_3\text{P}$ with HCl in dioxan at 25°; $a = 0.00861\text{M}$; $b = 0.335$ (A), 0.251 (B), 0.209 (C), 0.200 (D), 0.143 (E), or 0.0857M (F)

method, was shown to be negligible with the primary alkyl esters under these conditions. Tri-*n*-butyl phosphite was examined in the greatest detail as the rate of its reaction with hydrogen chloride was the most convenient for purposes of periodic sampling and titration. Second-order kinetics with respect to hydrogen chloride were demonstrated in experiments involving an excess ($\geq 10:1$ molar) of tri-*n*-butyl phosphite (Figure 1) (*cf.* ref. 9). The order with respect to phosphite (first) was determined from the best plot of the logarithm of the pseudo-second-order constant against the logarithm of phosphite concentration (Figure 2). For the other phosphites (Me, Et, and Prⁿ)

¹⁴ Farbenfabriken Bayer Akt.-Ges., B.P. 749,550/1956.

¹⁵ W. Gerrard, M. J. D. Isaacs, G. Machell, K. B. Smith, and P. L. Wyvill, *J. Chem. Soc.*, 1953, 394.

observed rates were too high for convenient measurement when high phosphite:hydrogen chloride ratios

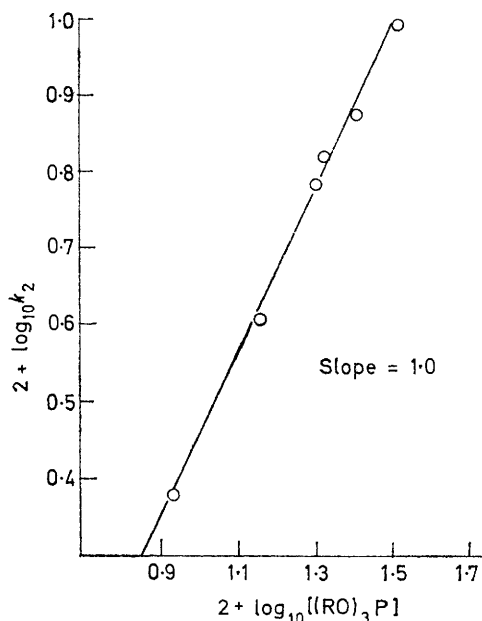


FIGURE 2 Determination of order in phosphite for the interaction of $(\text{BuO})_3\text{P}$ and HCl in dioxan at 25° (data from Table 6)

were employed. In these cases, and also in a number of experiments with tri-n-butyl phosphite, the overall

dealkylation of tri-n-butyl phosphite varied with the initial relative concentrations of reactants, and reached a maximum for phosphite:hydrogen chloride molar concentration ratios of 10:1 or higher. A possible explanation is that the order in hydrogen chloride varies, being on average greater than two unless

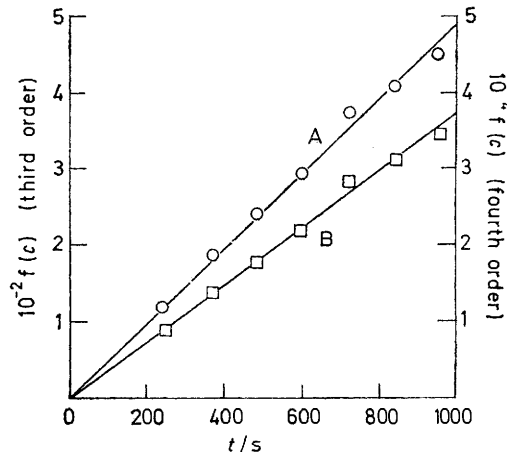


FIGURE 3 Overall third-order (A) and fourth-order (B) plots (see footnotes to Table 6) for interaction of HCl ($a = 0.0558\text{M}$) and $(\text{EtO})_3\text{P}$ ($b = 0.0967\text{M}$) in dioxan at 25°

a large excess of phosphite is present.^{16,17} For phosphite:hydrogen chloride initial concentration ratios of $<10:1$ it was impossible to distinguish between third- and fourth-order processes. Calculations of root

TABLE 6

Observed third- and fourth-order rate constants for the reactions of tri-methyl, -ethyl, -n-propyl, and -n-butyl phosphites with hydrogen chloride in dioxan at 25°

R in $(\text{RO})_3\text{P}$	Initial $[(\text{RO})_3\text{P}]$ (M)	Initial molar ratio $(\text{RO})_3\text{P} : \text{HCl}$	$10^2 k_3^a$		k_4^b	
			Mean $(1^2 \text{ mol}^{-2} \text{ s}^{-1})$	R.m.s. deviation (%)	Mean $(1^3 \text{ mol}^{-3} \text{ s}^{-1})$	R.m.s. deviation (%)
Me	0.0728	1.60	18.8	2.9	13.6	4.1
Et	0.141	1.62	10.4	5.6	6.06	5.8
Pr ⁿ	0.133	2.04	7.74	6.0	3.69	4.9
Bu ⁿ	0.147	1.55	7.19	11.7	4.40	14.2
Bu ⁿ	0.149	2.07	8.54	11.1	3.70	6.3
Bu ⁿ	0.112	5.69	15.4	5.0	12.7	9.4
Bu ⁿ	0.223	5.69	11.2	8.5	4.8	3.7
Bu ⁿ	0.186	9.50	18.7	11.5	14.2	4.6
Bu ⁿ	0.0857	9.95	28.8 ^c			
Bu ⁿ	0.143	16.6	28.8 ^c			
Bu ⁿ	0.200	23.2	29.2 ^c			
Bu ⁿ	0.209	24.3	31.0 ^c			
Bu ⁿ	0.251	29.4	30.0 ^c			
Bu ⁿ	0.335	38.9	30.8 ^c			

^a Calculated from $k_3 t = \frac{1}{(b-a)} \left[\frac{x}{a(a-x)} + \frac{1}{(b-a)} \log_e \frac{b(a-x)}{a(b-x)} \right]$, unless otherwise specified.

^b Calculated from $k_4 t = \frac{1}{2(b-a)(a-x)^2} + \frac{1}{(b-a)^2(a-x)} - \frac{1}{(b-a)^2} \log_e \frac{b(a-x)}{a(b-x)} - \frac{1}{2(b-a)a^2} - \frac{1}{a(b-a)^2}$.

^c Calculated from pseudo $k_2/[(\text{RO})_3\text{P}]$ (Figure 1).

third-order rate constants were calculated from the integrated form of the third-order rate equation (Table 6). Although consistently good plots were obtainable up to 70% completion in each experiment, the absolute values of the observed third-order constants for the

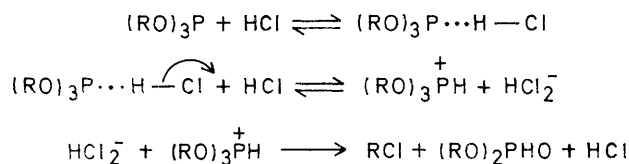
¹⁶ F. R. Mayo and J. J. Katz, *J. Amer. Chem. Soc.*, 1947, **69**, 1339.

mean square deviations for the third- and fourth-order rate constants showed that both fitted the data equally well.

It is likely that the second or third molecule of hydrogen chloride is necessary to 'solvate' the chloride

¹⁷ F. R. Mayo and M. G. Savoy, *J. Amer. Chem. Soc.*, 1947, **69**, 1348.

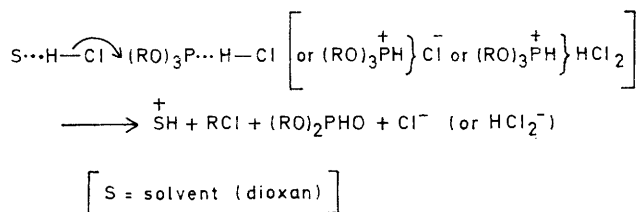
ion, possibly in the form of the hydrogen dichloride anion (Scheme 5).^{18,19}



SCHEME 5 †

† Although the *P*-protonated ester shown here and in Scheme 6 is the only species detectable by n.m.r., we cannot entirely exclude the possibility that rate limiting dealkylation involves the *O*-protonated phosphite which could co-exist in low concentration.

At the higher hydrogen chloride concentrations further solvation of HCl_2^- by hydrogen chloride in a less specific way might be involved. Alternatively, or additionally, hydrogen chloride could be involved in nucleophilic attack on the hydrogen-bonded or protonated species (Scheme 6).



SCHEME 6

No direct inference can be made from the observed relative rates for the Me, Et, Prⁿ, and Buⁿ esters. The rapidly reversible protonation which n.m.r. reveals, indicates however that R-O fission is the rate-limiting process. This is also suggested by the extremely slow rate of dealkylation of trineopentyl phosphite.

EXPERIMENTAL

Preparation and Purification of Materials.—Commercially obtained trialkyl phosphites were redistilled [R in (RO)₃P, b.p. (°C) at mmHg]: Me, 111–112 at 760; Et, 20–22 at 0.1; Buⁿ, 55–63 at 0.05–0.1. Tri-*n*-propyl phosphite, b.p. 35–37° at 0.1 mmHg, and trineopentyl phosphite, b.p. 76° at 0.2 mmHg, were prepared as described for the latter,¹ and di-*n*-propyl hydrogen phosphite, b.p. 42–45° at 0.1 mmHg, n_D^{20} 1.4175, by dealkylation of the triester with HCl.⁶ The purity of each was checked by ¹H and ³¹P n.m.r.

1,4-Dioxan was purified as described and distilled, b.p. 101–102°, from sodium.²⁰ Diethyl ether was sodium-dried. Sulphuric acid (100%) was kindly provided by Dr. R. F. M. White.

N.m.r. Spectroscopy.—¹H Spectra were recorded on a Perkin-Elmer R10 60 MHz spectrometer. ³¹P Spectra were mostly obtained by the pulsed Fourier transformation method on a Bruker HF 90 instrument operating at 36.4 MHz and equipped with a Nicolet Instrument Corporation computer series 1080. Quantitative ³¹P data for triphenyl phosphite–hydrogen chloride solutions were obtained on the continuous wave R10 instrument operating at 24.3 MHz. ³¹P Chemical shifts are relative to 85% phosphoric acid.

¹⁸ F. Kaufer and E. Kunz, *Ber.*, 1909, **42**, 385; T. C. Waddington, *J. Chem. Soc.*, 1958, 1708; Y. Pocker, *ibid.*, p. 240.

¹⁹ Y. Pocker, *J. Chem. Soc.*, 1960, 1292.

Coupling constants are within ± 6 (J_{PH}) or ± 0.7 Hz (J_{POCH_2}).

Phosphite–Hydrogen Chloride Solutions.—(a) *Trineopentyl phosphite.* Dried hydrogen chloride was passed into the phosphite dissolved in the appropriate solvent contained in a U tube fitted with taps and protected by drying tubes, until the required increase in weight was achieved. ³¹P Chemical shifts were recorded for a range of phosphite and hydrogen chloride concentrations in dioxan at 25° (Table 1) and in diethyl ether over the temperature range +25 to –70° (Table 2).

(b) *Triphenyl phosphite.* Dried hydrogen chloride was dissolved in neat triphenyl phosphite, as above. ³¹P N.m.r. at 33.5° showed each solution to contain (PhO)₃P, δ –126.7 p.p.m., and (PhO)₂PCL, δ –156.8 p.p.m., only. Integration yielded the results in Table 5.

(c) *Tri-*n*-butyl phosphite.* A solution in anhydrous ether, containing hydrogen chloride (1.1M) and the phosphite (4.4M) was prepared by mixing solutions of the two reactants at –70°. ³¹P N.m.r. showed the presence of the protonated phosphite, δ –25.2 p.p.m. (J_{PH} 834 Hz), as the main species present (>90%). No significant change occurred at –70° (15 min) or at –60° (25 min). At –50° dealkylation yielded di-*n*-butyl hydrogen phosphite, δ –8.0 p.p.m. (J_{PH} 703 Hz) (64% in 15 min; 93% in 30 min).

Reaction between Trifluoromethanesulphonic Acid and Trineopentyl Phosphite.—Trifluoromethanesulphonic acid (0.73 cm³, 7.3 mmol) was added slowly, under dry nitrogen, to trineopentyl phosphite (2.11 g, 7.2 mmol) at 0°. Anhydrous ether (20 cm³) was added, the solution was mixed well, and the ether was then removed under reduced pressure to leave a white solid which gradually yielded a colourless liquid at room temperature. The ³¹P spectrum of the initial product (in CDCl₃) showed two doublets centred at –23.6 and –11.5 p.p.m. with coupling constants (J_{PH}) of 834 and 744 Hz respectively. The former was assigned (Table 3) to protonated trineopentyl phosphite (70%) and the latter to protonated dineopentyl hydrogen phosphite (30%).

The spectra of solutions of trineopentyl phosphite and various excesses of trifluoromethanesulphonic acid were also recorded in CDCl₃ (ca. 10%) as lock (Table 3). Reactants were mixed at room temperature and the spectra recorded at 25° within 10 min of mixing.

Reaction between 100% Sulphuric Acid and Trineopentyl Phosphite.—The phosphite (0.5 g) was added to 100% H₂SO₄ (3 cm³) at 0°. Within 10 min the ³¹P spectrum at 25° showed three doublets, δ –19.8 (J_{PH} 810 Hz), –18.1 (J_{PH} 810 Hz), and –17.1 (J 804 Hz).

*Spectra of Di-*n*-propyl Phosphite in Trifluoromethanesulphonic Acid.*—Successive quantities of trifluoromethanesulphonic acid were added to the phosphite at room temperature and the ³¹P spectrum was recorded at 25°, immediately after each addition (Table 4).

Kinetic Experiments.—Stock solutions of anhydrous hydrogen chloride in dioxan, and of phosphites in dioxan, were prepared at 25° (thermostatted bath). HCl Solutions were standardized against 0.1M- or 0.01M-AgNO₃. Kinetic runs were started by mixing known volumes of stock solutions in a stoppered flask (25°). Samples (usually 10 cm³) were withdrawn by pipette at various intervals throughout the reaction and were immediately added to 6M-nitric acid (5 cm³); chloride ion was determined

²⁰ A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' Longmans, London, 1956, 3rd edn., p. 177.

potentiometrically against AgNO_3 . Reactions were followed to between 60 and 75% completion and took 0.75–3 h. Between six and ten samples were taken in each run. G.l.c. analysis of products showed olefin formation to be negligible. Consecutive dealkylation occurred to an insignificant extent, *e.g.*, di-*n*-propyl phosphite underwent only 1.1% dealkylation by HCl in 18 h, under the conditions employed.

Treatment of Data.—Rate constants were calculated from the required integrated rate equations, in the form $kt = f(c)$. See Figure 1 and the footnotes to Table 6, where in each case a and b are the initial concentrations of hydrogen

chloride and of phosphite respectively, and $(a - x)$ is the concentration of HCl after time t . The value of k for each time was calculated by computer and mean values were determined; results for samples taken at $t < 3$ min were excluded from calculations. Root mean square deviations for each run were calculated from $[\sum(X - \bar{X})^2/n]^{1/2}$ and expressed as a percentage of k (mean).

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