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Aggregation of Phosphoric Acid, Phenyl Dihydrogenphosphate, and Related Organophosphorus Acids in Conductometric Titration with Triethylamine in DMF

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The conductance increased linearly up to the equivalence point in the conductometric titration of diphenyl hydrogenphosphate ($(PhO)_2PO(OH)$) with triethylamine (Et_3N) in DMF at 25 °C. However, it was found that the conductometric titration of phenyl dihydrogenphosphate ($PhOPO(OH)_2$, 1.0×10^{-3}—1.0×10^{-2} mol dm^{-3}) gave a maximum at the half-equivalence point ($C_{HA} : [Et_3N] = 1 : 1/2$) and not the linear curve to the equivalence point. Phosphoric ($PO(OH)_3$), phenylphosphonic ($PhPO(OH)_2$), and vinylphosphonic ($CH_2CHPO(OH)_2$) acids also gave maxima at the half-equivalence points. The appearance of maxima was explained by homoconjugation between the acid (HA) and the conjugate anion (A^-) upon neutralization with the base (B) in DMF: $B+2\,HA \rightleftarrows BH^+\cdots HA_2{}^-$. Dibutyl hydrogenphosphate ($(n\text{-}BuO)_2PO(OH)$) of higher concentrations also gave a (small) maximum at the half-equivalence point, while dimethylphosphinic acid ($(CH_3)_2PO(OH)$) gave no maximum in DMF. In less basic solvents, acetonitrile and benzonitrile, even diphenyl hydrogenphosphate, gave a maximum. The cause for the appearance of maxima at the half-equivalence point in DMF is discussed from the viewpoint of the basicities of the conjugate anion (A^-) and the number of hydrogen bondings involved in the homoconjugation reaction. The ion-pair and quadrupole (the dimer of ion pairs) formation constants of the organophosphorus acids in DMF were obtained by conductometry. The equilibrium concentration of the dimer (H_2A_2) of $PhOPO(OH)_2$ was found to exceed that of the ion pair (HA) at $> 1.6\times10^{-3}$ mol dm^{-3} of the acid.

Titrations for acids and bases in non-aqueous solvents are often adopted, since acids and bases are highly differentiated in non-aqueous solvents.[1] The "clues" for speciation of the species in non-aqueous solvents have been provided[2] by conductometric titrations[3—5] as well as potentiometric titrations.[6] In a previous study,[7] we examined the conductometric titrations of fairly "strong" acids, i.e., sulfonic acids, such as *p*-toluenesulfonic and methanesulfonic acids, with amine bases in a low-solvating medium, benzonitrile and ethanol–benzonitrile mixtures. We attributed the maxima which appeared at the one-third equivalence point in the titration curve to a homoconjugation reaction between two molecules of acids (HA) and a conjugate base anion (A^-) upon neutralization with the base (B):

$$B+3\,HA \rightleftarrows BH^+\cdots A^-(HA)_2 \qquad (1)$$

The esters of phosphoric acid have been of interest because they serve as simple structural analogues of the phosphodiester network (C–O–P–O–C) in nucleic acids.[8] The dimerizations or polymerizations of organophosphorus acid compounds have been studied extensively,[9] not only in inert solvents,[10] but also in dipolar aprotic solvents,[11] such as acetone or nitrobenzene. The interactions between phosphoric acid diesters and bases in DMSO[12] and toluene[13] have been reported. The triple ion formation from n-$Bu_3NH^+(PhO)_2PO_2{}^-$ has been observed, even in acetonitrile and propylene carbonate,[14] and a strong dimerization reaction of $Na^+(PhO)_2PO_2{}^-$ in acetone has been observed conductometrically.[15]

In the present study, conductometric titrations with triethylamine were performed for mono- and diesters of phosphoric acid or phosphonic and phosphinic acids in DMF and other solvents at 25 °C. The appearance of maxima in the conductometric titration curves is reported; the tendency of homoconjugation reactions in DMF is discussed from the viewpoint of association constants of the acids and the number of hydrogen-bondings involved in the interaction between the acid (HA) and the conjugate base anion (A^-).

The ion-pair and quadrupole (or dimerization) formation constants of the acids can be determined by conductometry at 25 °C with our analytical method,[14—16] as follows: the association of an acid (HA) is expressed by

$$H^+ + A^- \rightleftarrows HA, \qquad Q_1 = K_1^a f_\pm^2 = \frac{[HA]}{[H^+][A^-]}, \qquad (2)$$

and the quadrupole formation (dimerization of the ion-pairs) is expressed by

$$2\,HA \rightleftarrows H_2A_2, \qquad Q_{41} = K_{41}^a = \frac{[H_2A_2]}{[HA]^2}. \qquad (3)$$

The mass balance for H^+ is

$$C_{HA} = [H^+] + [HA] + 2\,[H_2A_2], \qquad (4)$$

where C_{HA} is the analytical concentration of the acid. The concentration of (hydrogen-bonded) triple ions may be low enough to be ignored. Equations 2, 3, and 4 give a fourth-order equation,

$$2\,Q_{41}Q_1^2X^4+Q_1X^2+X-C_{\mathrm{HA}}=0. \qquad (5)$$

Equation 5 can be solved by Newton's method, or related methods. The concentrations of the the simple ion, the ion pair, and the quadrupole are given by $[\mathrm{H}^+]=[\mathrm{A}^-]=X$, $[\mathrm{HA}]=Q_1X^2$, and $[\mathrm{H_2A_2}]=Q_{41}{Q_1}^2X^4$, respectively. The whole molar conductivity is expressed by $\Lambda=\Lambda_o'X/C_{\mathrm{HA}}$. The effects of the ionic atmosphere on the limiting molar conductivity are corrected by Onsager's limiting equation, $\Lambda_o'=\Lambda_o-(\alpha\Lambda_o+\beta)\sqrt{I}$, where $\alpha=0.7165$ and $\beta=99.07$ for DMF at 25 °C;[17] and I is the ionic strength. Activity coefficients of ions were estimated by the Debye–Hückel equation with $A=1.593$, $B=0.4807\times10^{-8}$, [17] and $a=4$ Å.

Experimental

Commercially obtained *N*,*N*-dimethylformamide (DMF) and dimethy sulfoxide (DMSO) from Wako of GR grade were distilled under reduced pressure. The specific conductance of the purified DMF was ca. 9×10^{-8} S cm^{-1}. The purifications of acetonitrile,[16] acetone,[15] and ethanol[18] were described previously. Triethylamine (Wako, GR grade >99%), γ-collidine (Wako, GR grade >98%), 1,1,3,3-tetramethylguanidine (Wako), tetramethylammonium hydroxide (Wako, GR grade 15% aqueous solution) were used as received. Phosphoric acid ($\mathrm{PO(OH)_3}$, Aldrich, crystals >98%), phenyl dihydrogenphosphate ($\mathrm{PhOPO(OH)_2}$, TCI >99%), phenylphosphonic ($\mathrm{PhPO(OH)_2}$, TCI >99%), methylphosphonic ($\mathrm{CH_3PO(OH)_2}$, Aldrich 98%), and vinylphosphonic ($\mathrm{CH_2CHPO(OH)_2}$, Aldrich 97%) acids were used without further purification. Dibutyl ((n-BuO)$_2$PO(OH), TCI >97%) and diphenyl ($\mathrm{(PhO)_2PO(OH)}$, TCI >99%) hydrogenphosphates, dimethylphosphinic acid ($\mathrm{(CH_3)_2PO(OH)}$, Aldrich 97%), and (±)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate ($\mathrm{(C_{10}H_6)_2O_2PO(OH)}$, Aldrich 95%) were used as received.

Phenyl tetrabutylammonium hydrogenphosphate (n-$\mathrm{Bu_4N^+}$ $\mathrm{PhOPO(OH)(O^-)}$) was prepared by neutralization between phenyl dihydrogenphosphate in methanol and n-$\mathrm{Bu_4NOH}$ (Wako, GR grade 10% aqueous solution) in a 1 : 1 equivalent amount. White crystals were obtained by evaporation under a reduced pressure at <50 °C after the successive addition of methanol, acetone, and diethyl ether. The crystals were washed with diethyl ether several times, and dried in vacuo at 50 °C over $\mathrm{P_2O_5}$. Tetrabutylammonium phenylphosphonate (n-$\mathrm{Bu_4N^+PhPO(OH)(O^-)}$) and diphenyl phosphate (n-$\mathrm{Bu_4N^+(PhO)_2PO(O^-)}$) were prepared in a similar way. Commercially obtained tetrabutylammonium dihydrogenphosphate (n-$\mathrm{Bu_4N^+PO(OH)_2(O^-)}$, Aldrich 97%) was dried in vacuo at 70 °C over $\mathrm{P_2O_5}$. Perchloric acid (Wako, GR grade 70%) was diluted by DMF after titration with a standardized NaOH solution. The preparation and purification methods of n-$\mathrm{Bu_4NClO_4}$ were mentioned previously.[18]

Conductometric titrations were performed in a Yanagimoto conductivity cell (Type A: a cell constant of 0.5142) with a Hewlett Packard LCR meter (Model 4263A) under an $\mathrm{N_2}$ atmosphere at 25±0.02 °C. To a 25 ml acid solution, 25 µl aliquots of a hundred-fold concentration of an amine base was added using a Hamilton gas-tight microsyringe. For obtaining the association constants, the conductivities of the acids themselves were measured in a Yanagimoto conductivity cell (type C: a cell constant of 0.3942).

Results and Discussion

Appearance of Maxima and Homoconjugation Reactions. Figure 1 shows the conductometric titration curves of various concentrations of phenyl dihydrogenphosphate ($\mathrm{PhOPO(OH)_2}$, 25 ml) with hundred-fold concentrations of triethylamine in DMF. The conductances increased with increasing concentration of $\mathrm{Et_3N}$ up to the half-equivalence point, and then gradually decreased upon a further addition of triethylamine; the (first) equivalence points (all 250 µl) were not observed. Even for a concentration as low as 1.0×10^{-3} mol dm^{-3} of $\mathrm{PhOPO(OH)_2}$, the maximum around the half-equivalence point was observed. The appearance of the maximum suggested that phenyl dihydrogenphosphate could cause homoconjugation reactions in DMF.

Phenylphosphonic acid ($\mathrm{PhPO(OH)_2}$) of 1.0×10^{-3} to 1.0×10^{-2} mol dm^{-3} also gave a maximum at the half-equivalence point without indicating the equivalence point (cf. Fig. 2), although each conductance value for $\mathrm{PhPO(OH)_2}$ was smaller than that for phenyl dihydrogenphosphate ($\mathrm{PhOPO(OH)_2}$). For 5.0×10^{-3} mol dm^{-3} vinylphosphonic acid ($\mathrm{CH_2CHPO(OH)_2}$), a maximum just after the half-equivalence point was observed. The conductance of 5.0×10^{-3} mol dm^{-3} phosphoric acid ($\mathrm{PO(OH)_3}$ crystals) reached its maximum at the half-equivalence point, and decreased thereafter, although the concentration of 1.0×10^{-3} mol $\mathrm{PO(OH)_3}$ increased towards the (first) equivalence point without a maximum. Methylphosphonic acid (5.0×10^{-3} or 1.0×10^{-2} mol dm^{-3}) gave a broad maximum after the half-equivalent point in DMF.

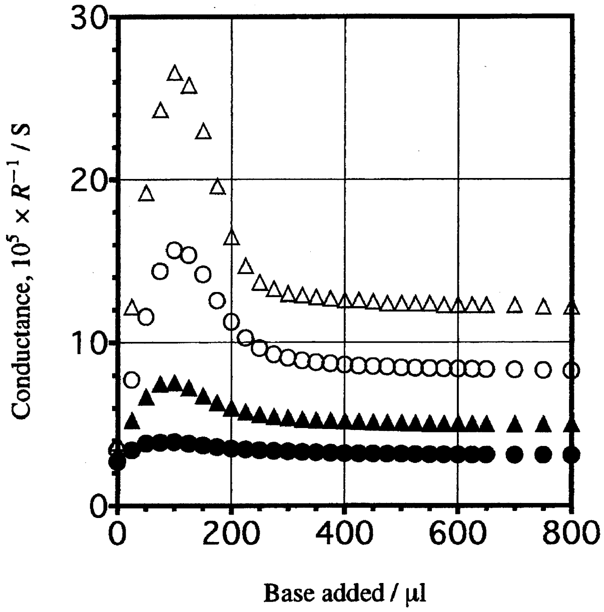


Fig. 1. Conductometric titration curves for various concentrations of phenyl dihydrogenphosphate (25 ml) with triethylamine in DMF at 25 °C: concentrations of the acid and added base are (△) 1.0×10^{-2} and 1.0 mol dm^{-3}, (○) 5.0×10^{-3} and 0.50 mol dm^{-3}, (▲) 2.0×10^{-3} and 0.20 mol dm^{-3}, and (●) 1.0×10^{-3} and 0.10 mol dm^{-3}, respectively.

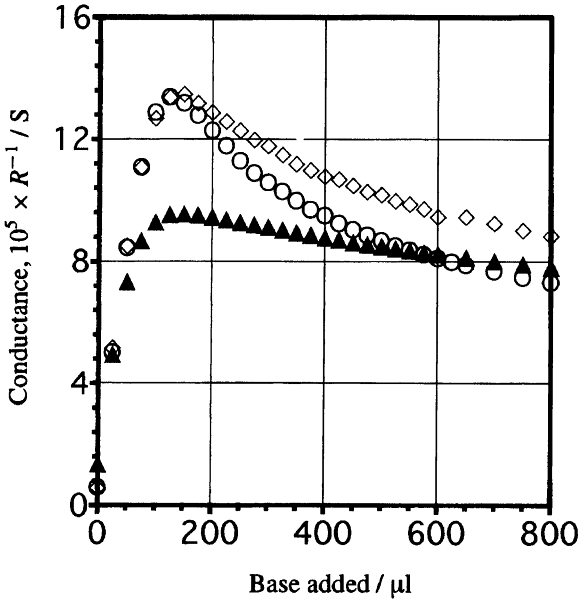


Fig. 2. Conductometric titration curves of 5.0×10^{-3} mol dm^{-3} solutions of (◇) vinylphosphonic acid, (○) phenylphosphonic acid, and (▲) phosphoric acid with 0.50 mol dm^{-3} triethylamine in DMF at 25 °C.

On the other hand, when a phosphoric acid diester, diphenyl phosphate ($(PhO)_2PO(OH)$) of 1.0×10^{-3} to 1.0×10^{-2} mol dm^{-3}, was titrated conductometrically with Et_3N, the conductance increased monotonically up to the equivalence point, and remained constant thereafter (cf. Fig. 3). However, an aliphatic-diester, dibutyl hydrogenphosphate ($(n\text{-}BuO)_2PO(OH)$), gave a small maximum just after the half-equivalence point, though the acid (diester) of a lower concentration (1.0×10^{-3} mol dm^{-3}) did not. The conductance values ($<6\times10^{-5}$ S) for 5.0×10^{-3} mol dm^{-3} $(n\text{-}BuO)_2PO(OH)$ after the equivalence point were much smaller than those for $(PhO)_2PO(OH)$ ($>20\times10^{-5}$ S); this indicated that the association between Et_3NH^+ and $(n\text{-}BuO)_2PO_2^-$ was larger than that between Et_3NH^+ and $(PhO)_2PO_2^-$. Dimethylphosphinic acid, $(CH_3)_2PO(OH)$ did not give a maximum. The conductances for $(CH_3)_2PO(OH)$ were much smaller than those for $(PhO)_2PO(OH)$ in the whole titration, indicating a larger association of dimethylphosphinic acid in DMF. For an aromatic phosphinic acid, (±)-1,1′-binaphthyl-2,2′-diyl hydrogen phosphate ($(C_{10}H_6)_2O_2PO(OH)$), the conductance changes were similar to those of $(PhO)_2PO(OH)$.

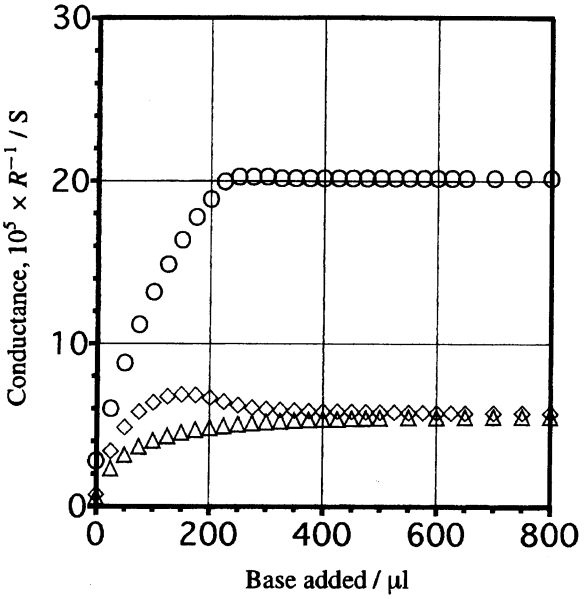


Fig. 3. Conductometric titration curves of 5.0×10^{-3} mol dm^{-3} solutions of (○) diphenyl hydrogenphosphate, (◇) dibutyl hydrogenphosphate, and (△) dimethylphosphinic acid with 0.50 mol dm^{-3} triethylamine in DMF at 25 °C.

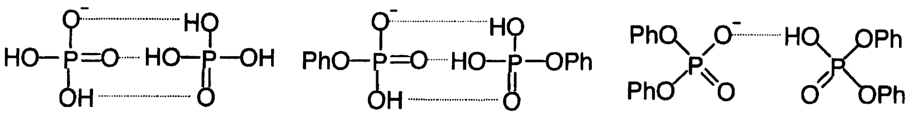
The appearance of maxima at the half-equivalence point in the conductometric titration of acid (HA) with an amine base (B) in aprotic solvents has been explained by a homoconjugation reaction between HA and A^- upon neutralization,

$$B + 2\,HA \rightleftarrows BH^+\cdots HA_2^- . \qquad (6)$$

In DMF, the formation constants of the homoconjugation reactions of some acids have been regarded as being small.[2] Gutmann's donor number of DMF (26.6) is a fairly large value, while the acceptor number of the solvent (16) is smaller than that of MeCN (19.3).[19] However, phosphoric acid and phenyl dihydrogenphosphate in DMF may form strong homoconjugated species through triple hydrogen-bondings (Scheme 1).

On the other hand, diphenyl hydrogenphosphate ($(PhO)_2POOH$) can combine with the conjugate base anion ($(PhO)_2PO_2^-$) through merely a single hydrogen-bonding; therefore, the homoconjugation reactions may not be strong enough to give a maximum in the titration curve. Even in DMF, however, the homoconjugation reaction of a phosphoric acid diester, dibutyl hydrogenphosphate ($(n\text{-}BuO)_2PO(OH)$), was strong enough to give a maximum. The difference between $(n\text{-}BuO)_2PO(OH)$ and $(PhO)_2PO(OH)$ may lie in the difference of association constants of the acids, in other words, the difference in the basicities of the conjugate anion (A^-). The association constants of these acids are given by means of conductometry in the next section.

In acetonitrile (DN=14.4 and AN=19.3),[19] a less basic medium, diphenyl hydrogenphosphate (1.0×10^{-3}—1.0×10^{-2} mol dm^{-3}), gave a maximum at the half-equivalence point (cf. Fig. 4), and phenyl dihydrogenphosphate gave very large maxima just before the equivalence point.



Scheme 1. Homoconjugation between HA and A^-.

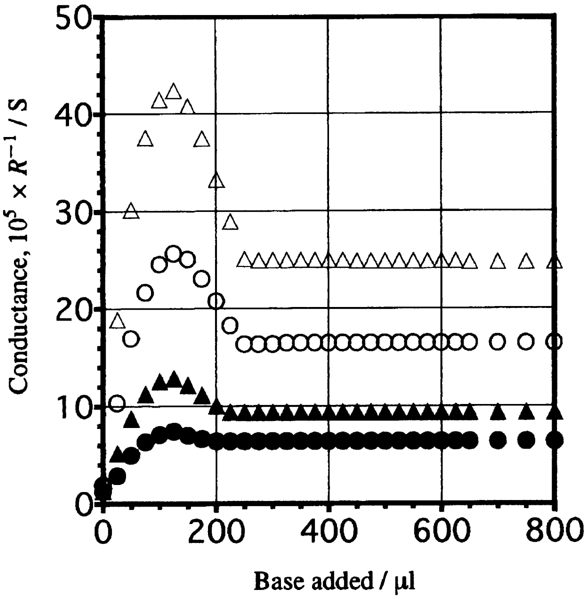


Fig. 4. Conductometric titration curves for various concentrations of diphenyl hydrogenphosphate (25 ml) with triethylamine in MeCN at 25 °C: concentrations of the acid and added base are (△) 1.0×10^{-2} and 1.0 mol dm^{-3}, (○) 5.0×10^{-3} and 0.50 mol dm^{-3}, (▲) 2.0×10^{-3} and 0.20 mol dm^{-3}, and (●) 1.0×10^{-3} and 0.10 mol dm^{-3}, respectively.

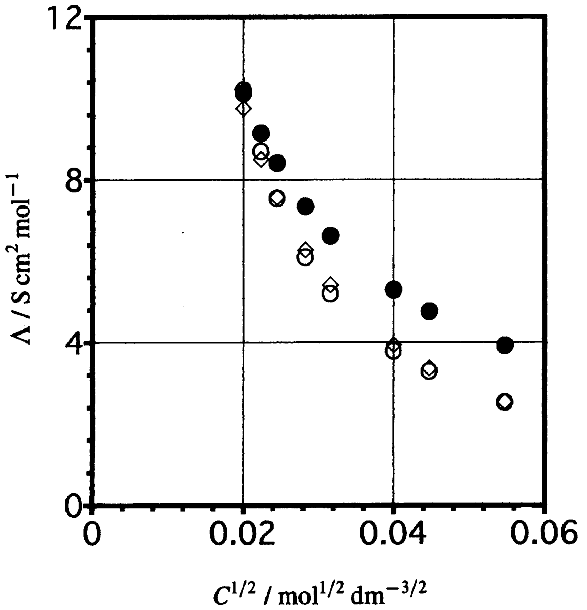


Fig. 5. Observed and calculated Λ_o values of phenyl dihydrogenphosphate in DMF at 25 °C: (○) observed; (●) calculated with the ion-pair formation alone, $K_1=9.5\times10^4$; (◇) calculated with the ion-pair and quadrupole formation, $K_1=5.8\times10^4$, $K_{41}=2.0\times10^3$, and $\Lambda_o=67.2$.

In acetone (DN=17.0 and AN=12.5),[19] 1.0×10^{-3} mol or 2.0×10^{-3} mol dm^{-3} (PhO)$_2$PO(OH) gave a maximum at the half-equivalence point (125 μl of Et$_3$N), whereas the occurrence of the maximum was delayed (ca. 150 μl) by the higher concentrations (5.0×10^{-3} and 1.0×10^{-2} mol dm^{-3}) of the phosphoric acid diester. On the other hand, 5.0×10^{-3} mol dm^{-3} PhOPO(OH)$_2$ gave a large maximum at 100 μl of 0.5 mol dm^{-3} Et$_3$N in the solvent. In a lesser basic solvent, benzonitrile (DN=11.9 and AN=15.5),[19] the maxima were observed at 150 μl and 75 μl of 0.50 mol dm^{-3} Et$_3$N for 5.0×10^{-3} mol dm^{-3} (PhO)$_2$PO(OH) and PhOPO(OH)$_2$, respectively.

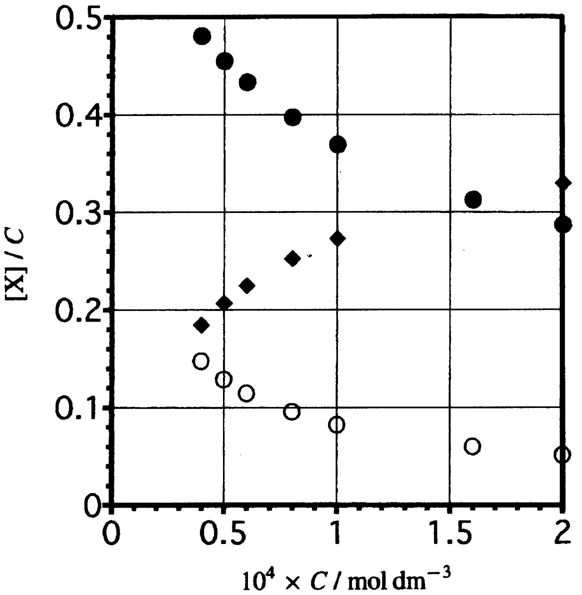


Fig. 6. Ratio of the equilibrium concentration ([X]) of species to the analytical concentration (C) of phenyl dihydrogenphosphate ($K_1=5.8\times10^4$ and $K_{41}=2.0\times10^3$) in DMF: (○) simple ions, [H$^+$]=[A$^-$]; (●) the ion pair, [HA]; (◆) the quadrupole, [H$_2$A$_2$].

In ethanol, the equivalence point was clearly observed (linear increase and sudden decrease in conductance) in the conductometric titration of PhOPO(OH)$_2$ with Et$_3$N, while phosphoric acid gave a convex curve up to the equivalence point and a horizontal line thereafter. In the titration of PO(OH)$_3$ with 1,1,3,3-tetramethylguanidine, a clear (first) end point was observed. With Me$_4$NOH, although a clear first neutralization point of PO(OH)$_3$ was observed, the second one was not clear. In DMSO, the conductances of PhOPO(OH)$_2$, (PhO)$_2$PO(OH), and (CH$_3$)$_2$PO(OH) only increased gradually with the addition of γ-collidine (2,4,6-trimethylpyridine); therefore, the end points were not given. The solubilities of amines, such as Et$_3$N or n-Bu$_3$N, in DMSO were too low to perform titrations with amines. By the way, a conductometric titration of phenylarsonic acid, PhAsO(OH)$_2$, with Et$_3$N in DMF gave a convex curve without indicating the equivalence point.

Dimerization of Organophosphorus Acids in DMF. In the previous section, it was described that phosphoric acid (PO(OH)$_3$), phenyl dihydrogenphosphate (PhOPO(OH)$_2$), and phenylphosphonic acid (PhPO(OH)$_2$) gave maxima at the half-equivalence point in the conductometric titration curves with triethylamine in DMF, whereas diphenyl hydrogenphosphate ((PhO)$_2$PO(OH)) or dimethylphosphinic acid ((CH$_3$)$_2$PO(OH)) did not. The higher concentrations of di-

Table 1. The Limiting Molar Conductivities (Λ_o) and K_a Values by the Direct Shedlovsky Analysis of the Organophosphorus Acids and the Intrinsic Λ_o Values Calculated with Strong Electrolytes in DMF at 25 °C

Acids or Salts	Shedlovsky		Kohlrausch[a)]
	Λ_o	K_a[b)]	Λ_o
Phosphoric acid	(−1.17)	(1.45×10^3)	73.5
Phenyl dihydrogenphosphate	(−4.38)	(1.59×10^3)	67.2
Phenylphosphonic acid	(−1.99)	(1.21×10^3)	67.5
Diphenyl hydrogenphosphate	(−7.69)	(2.23×10^3)	64.8
Dibutyl hydrogenphosphate[c)]	(−2.35)	(1.10×10^3)	66[d)]
$HClO_4$	86.4	3.39	
n-Bu_4NClO_4	77.2	1.78	
n-$Bu_4N^+PO(OH)_2(O^-)$	64.3	65.4	
n-$Bu_4N^+PhOPO(OH)(O^-)$	58.0	10.1	
n-$Bu_4N^+PhPO(OH)(O^-)$	58.3	25.9	
n-$Bu_4N^+(PhO)_2PO(O^-)$	55.6	15.2	

a) $\Lambda_o(HA)=\Lambda_o(HClO_4)+\Lambda_o(n\text{-}Bu_4NA)-\Lambda_o(n\text{-}Bu_4NClO_4)$. b) Association constant, $H^+ + A^- \rightleftarrows HA$ or $M^+ + A^- \rightleftarrows MA$, by the Shedlovsky analysis. c) The Shedlovsky analysis was applied for the 10 points of 3.65×10^{-4}—3.45×10^{-3} mol dm^{-3}, see the text for other acids. d) A predicted value.

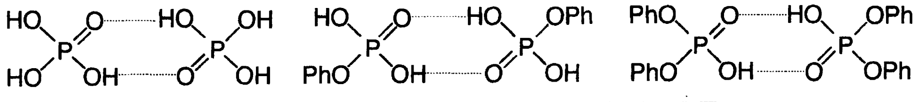
butyl hydrogenphosphate ($(n\text{-}BuO)_2PO(OH)$) also gave a (small) maximum in DMF. The association constants of these organophosphorus acids in DMF are obtained by means of conductometry.

Figure 5 shows the observed molar conductivities (Λ/S cm^2 mol^{-1}) of phenyl dihydrogenphosphate over the concentration range of 4.0×10^{-4}—3.0×10^{-3} mol dm^{-3} in DMF. A direct analysis with the Shedlovsky method[20)] using lower concentrations (1.8×10^{-4}—1.7×10^{-3} mol dm^{-3}) of the acid monoester gave a "negative" Λ_o value of −4.38 and a "pseudo" association constant (K_a) of 1.59×10^3 (cf. Table 1). The intrinsic Λ_o value was evaluated by Kohlrausch's additivity law with "strong" electrolytes: $\Lambda_o(HA)=\Lambda_o(HClO_4)^{21)}+\Lambda_o(n\text{-}Bu_4NA)-\Lambda_o(n\text{-}Bu_4NClO_4)$. The observed Λ values of 18.5 to 3.59 used for the Shedlovsky analysis seemed to be high enough to evaluate a precise Λ_o value. The failure of the Shedlovsky analysis can be attributed to a higher aggregate formation above the 1 : 1 association in the solution. We have reported that the application of the Shedlovsky and related methods to some salts in aprotic solvents gives extremely large or (even) "negative" Λ_o values if strong quadrupole (dimer of ion-pairs) formations occur in the solution.[7,15,16)] The observed (after interpolation) Λ values in Fig. 5 could not be explained by 1 : 1 association: An ion-pair formation constant (K_I) of 9.5×10^4 gave a relative error of −0.78 and +54.9% to the observed Λ values at 4.0×10^{-4} and 3.0×10^{-3} mol dm^{-3}, respectively, of phenyl dihydrogenphosphate. However, the combination of K_I (5.8×10^4) and K_{41} (2.0×10^3: quadrupole formation) explained the whole observed Λ values (4.0×10^{-4}—3.0×10^{-3} mol dm^{-3}) with a relative error of −4.25—+4.21%. The inclusion of (hydrogen-bonded) triple ion formation might improve the calculation results. However, the strong quadrupole formation prevented us from evaluating an adequate constant of triple ion formation (from the acid). It has been found[7,15)] that the

Table 2. Ion-Pair (K_I) and Quadrupole (K_{41}) Formation Constants of the Organophosphorus Acids in DMF at 25 °C

Acids	K_I	K_{41}	Rel. error[a)]/%	σ_{error}[b)]	$10^3\times\Delta C$/mol dm^{-3}
Phosphoric acid	8.4×10^5	2.4×10^3	−2.73—+3.23	2.43	0.4—3.0
Phenyl dihydrogenphosphate	5.8×10^4	2.0×10^3	−4.25—+4.21	3.07	0.4—3.0
Phenylphosphonic acid	1.31×10^5	5.5×10^3	−4.26—+4.05	2.95	0.4—3.0
Diphenyl hydrogenphosphate	3.1×10^4	1.3×10^3	−4.78—+2.66	2.90	0.4—3.0
Dibutyl hydrogenphosphate[c)]	1.4×10^5	1.45×10^3	−3.08—+2.92	2.00	0.8—4.0

a) The relative error in the calculated Λ value to the observed Λ value for the whole concentration range, e.g., $\Delta C=(0.4-3.0)\times10^{-3}$ mol dm^{-3}. b) Standard deviation of the relative error. c) A predicted Λ_o value of 66 was used for the evaluation of K_I and K_{41}. The use of another Λ_o value, 65, gave similar K_I and K_{41} values.



Scheme 2. Dimerization of phosphoric acids in DMF.

equilibrium concentrations of triple ions remain very low, compared with those of single ions, by the inclusion of considerably large constants of triple ion formation when the quadrupole formation governs the reaction in the solution.

The concentrations of the species present in the solution were evaluated. Figure 6 shows the ratio of the species ([X]) to the analytical concentration (C) of phenyl dihydrogenphosphate (HA) in DMF. The ratio ($[A^-]/C$) of simple ions ($[H^+]=[A^-]$) decreased from 0.148 to 0.0515 with increasing C of 4.0×10^{-4} to 3.0×10^{-3} mol dm^{-3}. Even the equilibrium concentration ratio ($[HA]/C$) of HA decreased with increasing C. The concentration ratio of the quadrupole ($[H_2A_2]/C$) increased from 0.185 to 0.330 with increasing C of 4.0×10^{-4} to 3.0×10^{-3} mol dm^{-3}.

Phosphoric and phenylphosphonic acids, as well as diphenyl and dibutyl phosphates, were examined in a similar way; the obtained ion-pair and quadrupole formation constants are listed in Table 2. The order of the K_1 values decreased as $PO(OH)_3$ (8.4×10^5) > (n-BuO)$_2$PO(OH) ≧ PhPO(OH)$_2$ > PhOPO(OH)$_2$ > (PhO)$_2$PO(OH) (3.1×10^4); the K_{41} values were PhPO(OH)$_2$ (5.5×10^3) > PO(OH)$_3$ > PhOPO(OH)$_2$ > (n-BuO)$_2$PO(OH) ≧ (PhO)$_2$PO(OH) (1.3×10^3). It has been reported[9,22] that the pK_a values of phosphoric acid, dibutyl and diphenyl hydrogenphosphates in H_2O are 2.12, 1.00, and 0.26, respectively; the dimerization constants of dibutyl and diphenyl hydrogenphosphates in chloroform are $10^{4.48}$ and $10^{3.76}$, respectively. The orders of the K_1 and K_{41} values in DMF are consistent with these reported values in H_2O and chloroform.

As shown above, the organophosphorus acids formed their dimers; the concentration of the dimer (H_2A_2: quadrupole) was found to exceed that of the ion-pair (HA) at $>1.6\times10^{-3}$ mol of PhOPO(OH)$_2$ in DMF at 25 °C. Scheme 2 shows the dimers of the phosphoric acids. Each phosphoric acid (non-, mono-, or diester) can form a dimer through double hydrogen-bondings; therefore, the dimerization constants may not differ from one another very much, as shown in Table 2. We point out that higher aggregations from (PhO)$_2$PO$_2^-$Li$^+$ and (PhO)$_2$PO$_2^-$Na$^+$ were not observed in DMF, while strong dimerization of (PhO)$_2$PO$_2^-$Na$^+$ in acetone has been reported.[15]

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