Structure and Basicity. Part 10.[1] Conductometric and Potentiometric Titrations of Some Cyclotriphosphazatrienes in Non-aqueous Media. The Conductivities of Alkali-metal Acetates on Titration with Perchloric Acid in Acetic Acid†

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Conductometric titrations of cyclotriphosphazatriene derivatives with perchloric acid in three solvent systems, (*i*) nitrobenzene, (*ii*) nitrobenzene–benzene (1 : 1), and (*iii*) acetic acid, are described and compared with potentiometric titrations in nitrobenzene using the same acid. Only the strongest bases can be titrated conductometrically in nitrobenzene. Acetic acid gives the largest range. The N-shaped curves in nitrobenzene–benzene (1 : 1) allow the best determinations of end-points for strong bases. The conductivities of the alkali-metal acetates in acetic acid on titration with perchloric acid are described. The shapes of the conductometric titration curves are discussed and a proton-jump mechanism is proposed for acetates in acetic acid.

It has been demonstrated earlier that valuable information can be gained by titrating cyclophosphazenes (and other compounds) with perchloric acid in nitrobenzene solution using a potentiometric technique.[1–15] We now extend the use of this technique, by comparing potentiometric titrations of cyclotriphosphazatrienes in nitrobenzene solution with conductometric titrations of these compounds (*i*) in nitrobenzene, (*ii*) in 1:1 molar mixtures of nitrobenzene and benzene, and (*iii*) in acetic acid, whose dielectric constants, ε, are 36, 19, and 6 respectively.

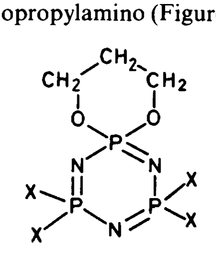
Results and Discussion

The data for four strongly basic cyclophosphazenes are presented in Table 1 and Figure 1(*a*) and (*b*)—(*d*) show the potentiometric and conductometric titration curves, respectively, for the hexapyrrolidino derivative, $N_3P_3(NC_4H_8)_6$. For these strongly basic cyclophosphazenes the conductometric curves in nitrobenzene, nitrobenzene–benzene (1:1), and acetic acid are chair-, N-, and boat(tub)-shaped respectively. Of these, the N-shaped curves allow the most accurate estimates of end-points. The potentiometric and conductometric measurements give two end-points corresponding to 1 and 2 equivalents of acid, respectively. In Table 2 the results for hexa(arylamino)-, $N_3P_3(NHR)_6$ (R = aryl), and alkylamino-chloro-cyclotriphosphazatrienes, $N_3P_3Cl_{6-n}(NR'R'')_n$ (R′ = alkyl, R″ = alkyl or H, n = 2, 3, or 4), and the derivatives $N_3P_3Cl_3(NC_4H_8)_3$ and $N_3P_3Cl_2(NC_5H_{10})_4$ (NC_5H_{10} = piperidino) are given. It was observed that $pK'_{a,1}$ values can be measured potentiometrically only for the stronger of these weak bases, and that conductometrically only one deflection is observed in acetic acid, two or one in nitrobenzene–benzene, and, except for $N_3P_3(NHC_6H_4Me\text{-}p)_6$, none in nitrobenzene. The weakest of the bases in Table 2 gives neither potentiometric nor conductometric end-points. The compound *trans*-$N_3P_3Cl_3(NC_4H_8)_3$ occupies an intermediate position.

In Table 3 other cyclotriphosphazatrienes are listed, spanning a range from very weakly basic to very strongly basic. The following observations were noted as the $pK'_{a,1}$ values, observed potentiometrically, increased. (*i*) Conductometrically, end-points are first observed in acetic acid. These change from one deflection with no minimum, to one deflection with a minimum, to two deflections with a boat shape. (*ii*) At higher $pK'_{a,1}$ values nitrobenzene–benzene (1:1) solutions begin to yield conductometric results. So far, only double deflections with chair and N shapes have been observed. (*iii*) Finally, for the most basic compounds, conductometric results are also observed in nitrobenzene solution.

With the present conductometric data, the following preliminary observations were made: (*i*) in acetic acid, single deflections at $pK'_{a,1} \geqslant -4$ and boat-shaped double deflections at $pK'_{a,1} \geqslant 6$; (*ii*) in nitrobenzene–benzene (1:1), chair-shaped double deflections for $pK'_{a,1} > 2.5$ and N-shaped double deflections at $pK'_{a,1} \geqslant 6$; and (*iii*) in nitrobenzene, single deflections at $pK'_{a,1} > 2.5$ and chair-shaped double deflections at $pK'_{a,1} > 6$.

Figures 2, 3, and 4 pertain to data for three different tetra-amino derivatives of the 1,3-dioxypropane spirophosphazene, $N_3P_3[O(CH_2)_3O]X_4$ [X = NHEt (Figure 2), morpholino (Figure 3), and cyclopropylamino (Figure 4)]. These derivatives differ by *ca.* 4 pK'_a units due to the differing base-strengthening effects of the three different amino residues. Their order of basicity is, as expected, X = NHEt > NC_4H_8O > NHC_3H_5, the last one containing a cyclopropylamino residue which behaves like an unsaturated amino group. In Figures 3(*d*) and 4(*c*) there is probably, and in Figure 3(*b*) possibly, a second end-point at 2 equivalents of acid. However, as blank experiments with perchloric acid in these solvents show a slight curvature, we cannot be absolutely certain on this point at this stage. With decreasing basicity, measured potentiometrically, the conductometric behaviour changes in the manner outlined above.



X = NHEt, NC_4H_8O, or NHC_3H_5

We now attempt to discuss the shapes of the conductometric curves. If no deflection is observed, the increased conductivity is due to the added acid which will protonate the solvent to give $MeCO_2H_2^+$ ions in acetic acid. The nitrobenzene system is discussed first. This solvent has the highest dielectric constant

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† *Non-S.I. unit employed:* mmHg ≈ 133 Pa.

Table 1. Potentiometric and conductometric data[a]

	Potentiometric[b] (nitrobenzene)		Conductometric[c]		
Compound	p$K'_{a,1}$	p$K'_{a,2}$	Nitrobenzene	Nitrobenzene–benzene (1 : 1)	Acetic acid
$N_3P_3(NMe_2)_6$	7.30	−3.35	C	N	B
	(7.5)	(−3.3)			
$N_3P_3(NEt_2)_6$	8.40	−4.30	C	N	B
	(8.5)	(−3.90)			
$N_3P_3(NC_4H_8)_6$	9.00	−1.40	C	N	B
$N_4P_4(NMe_2)_8$	8.25	0.45	C	N	B
	(8.3)	(0.6)			

[a] For all compounds the end-points occur at 1 and 2 equivalents of acid. [b] Lit.[3] values in parentheses. [c] The curve shapes are given by: for two end-points, B = boat shaped, C = chair shaped, N = N shaped; for one end-point, V = V shaped, P = plateau, A = ascent; for no end-point, L = linear.

Table 2. Potentiometric and conductometric data for $N_3P_3(NHR)_6$ (R = aryl), $N_3P_3Cl_{6-n}(NR'R'')_n$ (R′ = alkyl, R″ = alkyl or H, n = 2, 3, or 4), $N_3P_3Cl_2(NC_5H_{10})_4$, and $N_3P_3Cl_3(NC_4H_8)_3$

	Potentiometric[a] (nitrobenzene)	Conductometric[b]		
Compound	p$K'_{a,1}$	Nitrobenzene	Nitrobenzene–benzene (1 : 1)	Acetic acid
gem-$N_3P_3Cl_2(NHBu^t)_4$	4.60		A	V
	(3.50)			
$N_3P_3(NHC_6H_4Me$-*p*$)_6$	3.00	P	C	A
	(3.00)			
$N_3P_3(NHC_6H_4Me$-*m*$)_6$	2.25	L	C	A
$N_3P_3(NHPh)_6$	1.90	L	A	A
	(1.2)			
cis-$N_3P_3Cl_2(NC_5H_{10})_4$	−0.70	L	Not soluble	Not soluble
	(−0.90)			
trans-$N_3P_3Cl_3(NC_4H_8)_3$	−4.0		L	A
trans-$N_3P_3Cl_3(NMe_2)_3$	< −6.0		L	L
	(−5.4)			
$N_3P_3Cl_4[NH(CH_2)_3NH]$	< −6.0		L	L

[a] Lit.[5] values in parentheses. [b] See footnote *c*, Table 1.

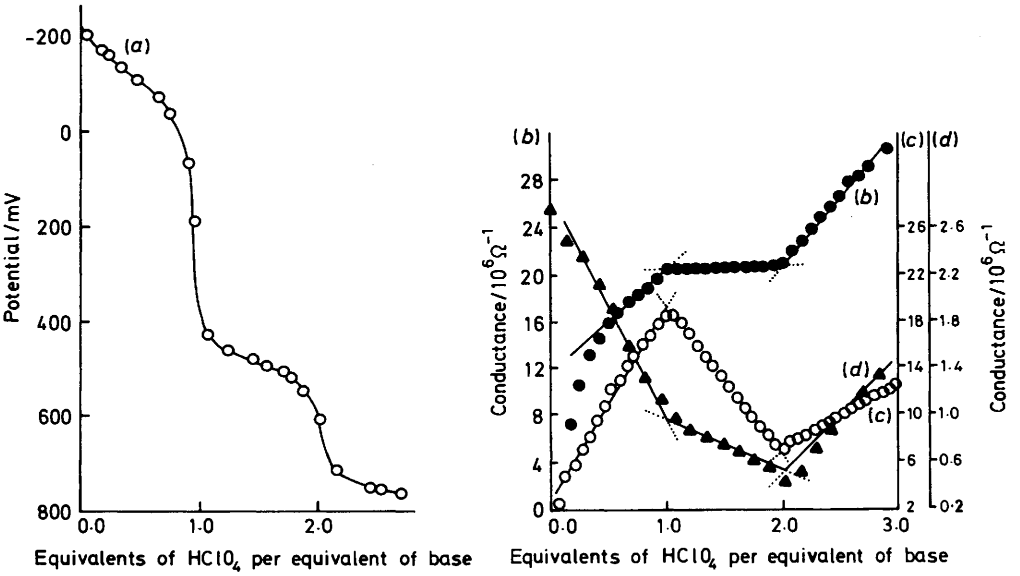

Figure 1. Titration curves for $N_3P_3(NC_4H_8)_6$: (*a*) potentiometric in nitrobenzene, (*b*) conductometric in nitrobenzene, (*c*) conductometric in nitrobenzene–benzene (1 : 1), and (*d*) conductometric in acetic acid

Table 3. Potentiometric and conductometric data for cyclotriphosphazatrienes covering a wide basicity range

Compound	Potentiometric (nitrobenzene) $pK'_{a,1}$	Conductometric: Nitrobenzene	Conductometric: Nitrobenzene–benzene (1:1)	Conductometric: Acetic acid
$N_3P_3Cl_6$	< -6	L	L	L
$N_3P_3[O(CH_2)_2O]Cl_4$	< -6		L	L
$N_3P_3[O(CH_2)_3O]Cl_4$	< -6		L	L
$N_3P_3[O(CH_2)_4O]Cl_4$	< -6		L	L
$N_3P_3[O(CH_2)_2NH]Cl_4$	< -6		L	L
$N_3P_3[O(CH_2)_3NH]Cl_4$	< -6		L	L
$N_3P_3[NH(CH_2)_2NH]Cl_4$	< -6		L	L
$N_3P_3[O(CH_2)_2O]_2Cl_2$	< -6			L
$N_3P_3[O(CH_2)_3O]_2Cl_2$	< -6			L
$N_3P_3[O(CH_2)_2O]_3$	-2.60		Not soluble	A
$N_3P_3[O(CH_2)_3O]_3$	-1.50		Not soluble	A
$N_3P_3[O(CH_2)_3O](NHC_3H_5)_4$	-1.43		L	A
$N_3P_3[O(CH_2)_4O]_3$	-0.28		Not soluble	A
$N_3P_3[O(CH_2)_3O](NC_4H_8O)_4$	2.67	P	C	V
$N_3P_3[O(CH_2)_3O](NC_4H_8)_4$	6.10	C	N	B
$N_3P_3[O(CH_2)_3O](NHEt)_4$	6.25	C	N	B

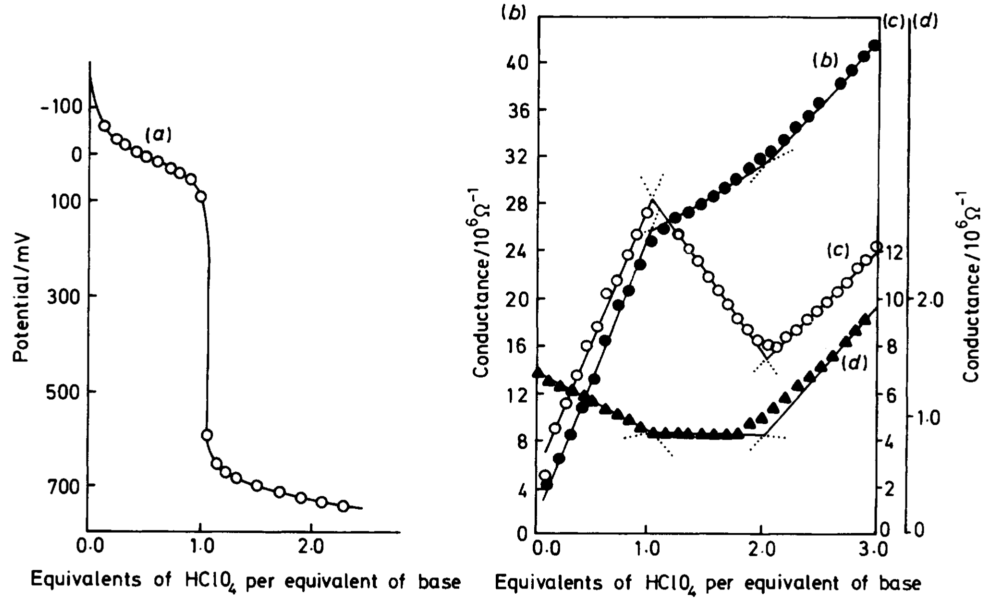

Figure 2. Titration curves for $N_3P_3[O(CH_2)_3O](NHEt)_4$: (*a*) potentiometric in nitrobenzene, (*b*) conductometric in nitrobenzene, (*c*) conductometric in nitrobenzene–benzene (1:1), and (*d*) conductometric in acetic acid

($\varepsilon = 36$) of the systems investigated. For the base B, a cyclophosphazene derivative, we can consider the equilibria (1)—(5) where species such as $HB^+ClO_4^-$ represent ion pairs.

$$B + HClO_4 \rightleftharpoons HB^+ClO_4^- \qquad (1)$$

$$HB^+ClO_4^- \rightleftharpoons HB^+ + ClO_4^- \qquad (2)$$

$$HB^+ + ClO_4^- + HClO_4 \rightleftharpoons H_2B^{2+}ClO_4^- + ClO_4^- \qquad (3)$$

$$H_2B^{2+}ClO_4^- + ClO_4^- \rightleftharpoons H_2B^{2+} + 2ClO_4^- \qquad (4)$$

$$H_2B^{2+}ClO_4^- + ClO_4^- \rightleftharpoons H_2B^{2+}2ClO_4^- \qquad (5)$$

Thus, for the chair-shaped curves with two deflections, as the conductivity increases to 1 equivalent of acid, then equilibrium (2) makes an important contribution. The second equivalent of acid changes the conductivity but little, possibly because of equilibrium (3) where one perchlorate ion is ion paired. After the addition of 2 equivalents of acid, an increase in conductivity is again observed due to the acid itself.

In the mixed solvent nitrobenzene–benzene (1:1), a medium of lower dielectric constant ($\varepsilon = 19$), it might be expected that ion pairing would become more important than in nitrobenzene. The N-shaped curves indicate that this is the case. During the addition of the first equivalent of acid the increase in conductivity again suggests the importance of equilibrium (2), but addition of the second equivalent results in a sharp decrease in conductivity, to which the equilibria (3) and (5) probably contribute.

In acetic acid ($\varepsilon = 6$), the medium of lowest dielectric constant considered here, the following additional equilibria (6)—(10) must be considered. If we consider the strongest bases first, we observe two deflections, and boat-shaped curves. The decrease in conductivity on the addition of the first equivalent of strong acid is perhaps due to a decrease in the proton-jump

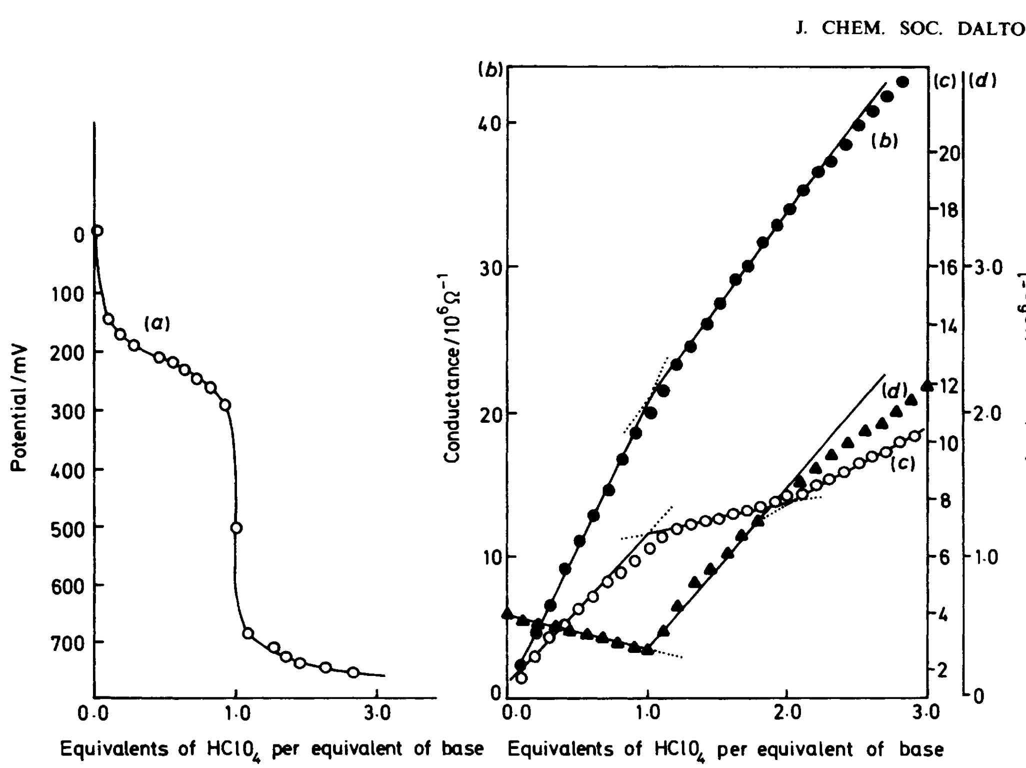

Figure 3. Titration curves for $N_3P_3[O(CH_2)_3O](NC_4H_8O)_4$: (*a*) potentiometric in nitrobenzene, (*b*) conductometric in nitrobenzene, (*c*) conductometric in nitrobenzene–benzene (1:1), and (*d*) conductometric in acetic acid

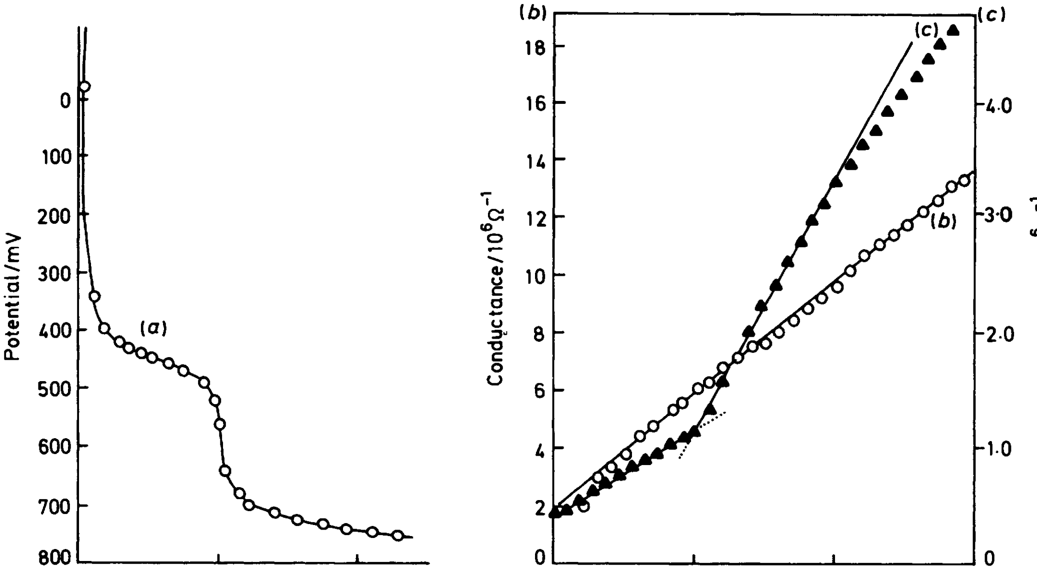

Figure 4. Titration curves for $N_3P_3[O(CH_2)_3O](NHC_3H_5)_4$: (*a*) potentiometric in nitrobenzene, (*b*) conductometric in nitrobenzene–benzene (1:1), and (*c*) conductometric in acetic acid

$$B + MeCO_2H \rightleftharpoons HB^+MeCO_2^- \quad (6)$$

$$HB^+MeCO_2^- \rightleftharpoons HB^+ + MeCO_2^- \quad (7)$$

$$MeCO_2^- + MeCO_2H \rightleftharpoons MeCO_2H + MeCO_2^- \quad (8)$$

$$HB^+MeCO_2^- + HClO_4 \rightleftharpoons HB^+ClO_4^- + MeCO_2H \quad (9)$$

$$HB^+ + MeCO_2^- + HClO_4 \rightleftharpoons HB^+ + ClO_4^- + MeCO_2H \quad (10)$$

mechanism (8). This mechanism (8), in turn, probably requires some contribution from equilibria (7) and (2). The overall decrease in conductivity, however, shows that the contribution from (2) is outweighed by the decrease in that of (7) and (8), as $MeCO_2^-$ ions are removed by (10). The second equivalent of acid results in only a slight decrease in conductivity. Hence, equilibrium (3) probably makes a major, and (5) a minor contribution. As the base strength of B is lowered, we observe only one deflection which, for the weakest bases, shows an increase in conductivity for the first equivalent of acid, followed by a sharper increase for the acid itself, presumably because

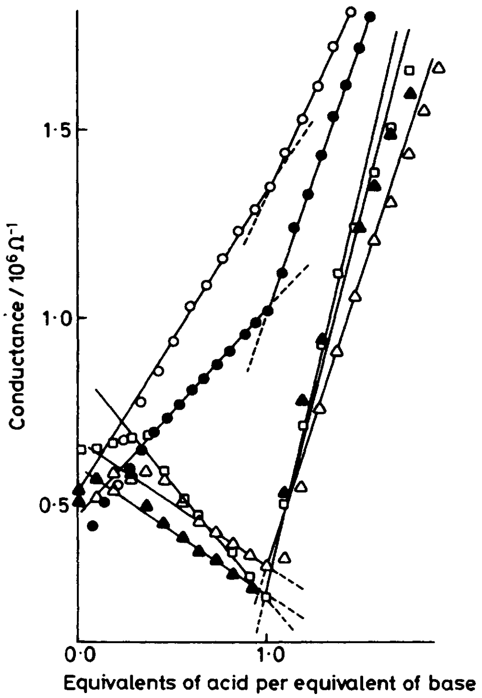

Figure 5. Conductometric titrations for alkali-metal acetates in acetic acid solvent: LiO_2CMe (○), NaO_2CMe (●), KO_2CMe (△), RbO_2CMe (▲), and CsO_2CMe (□)

equilibrium (2), from the strong acid considerably outweighs the equilibria (6) and (7), from the weak acid, and as (7) is only minor, its contribution to (8) and (10) would also be only minor.

Most simple carboxylic acids occur as hydrogen-bonded cyclic dimers in their crystals (except acetic acid, which forms an infinite polymer).[16] Monocarboxylic acids are also largely dimerised in non-polar solvents and at moderate temperatures in the vapour phase.[17] Pure acetic acid occurs as a dimer in the liquid phase over a wide temperature range.[17] Crystallisation of alkali-metal acetates from glacial acetic acid gives rise to acid salts, $MH(O_2CMe)_2$. These contain some of the strongest $O{-}H\cdots O$ hydrogen bonds known.[17] It is thus clear that acetate ions can disrupt the cyclic dimers and the postulated proton-jump mechanism seems feasible.

To obtain further evidence for this we have titrated the alkali-metal acetates MO_2CMe (M = Li, Na, K, Rb, or Cs) with perchloric acid in acetic acid solution (Figure 5). We note that the conductivities fall into two groups; for M = Li and Na they increase, for M = K, Rb, and Cs they decrease. For M = Li the conductivity increases sharply, almost as much as for $MeCO_2H_2^+$. For Na the increase is somewhat less. For M = K, Rb, and Cs the conductivity decreases, this decrease being more marked the larger the size of the alkali-metal cation. In aqueous solution the acetates are relatively highly dissociated, but systematic trends in the activity coefficients[18] point to a weak association between the alkali-metal ions and the acetate ion, decreasing in the order $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$. The same phenomenon is observed for other salts whose anions are strong Lewis bases, most notably the hydroxides, but not for salts of strong acids, like halides or perchlorates. Thus the acetate ion, being a stronger Lewis base than the water molecule, will tend to replace it in the primary solvation shell of the cation. However, this tendency will be offset by steric inhibition to solvation by the bulky ion, and the acetate ion may reside in a secondary solvation shell, exerting its effect through co-operative hydrogen bonding[19] with a water molecule in the primary shell, the 'localised hydrolysis' theory of Robinson and Harned.[20] Either way, the acid–base interaction will be stronger the smaller the cation.[20] In acetic acid solution, the same phenomenon should be observed. Since the replacement of a solvating acetic acid molecule in the primary solvation shell by an acetate ion now occurs without steric inhibition, the effect is presumably more marked.

We suggest that the above behaviour noted for the alkali-metal acetates in acetic acid can be rationalised by increased tightness of ion pairing with decreasing size of the alkali-metal cation. Hence, the larger the cation the more loosely bound the acetate ion and the greater its availability for a proton-jump mechanism.

Our data for cyclotriphosphazatrienes in acetic acid (Tables 1—3 and Figures 1—4) show behaviour mirroring that of the alkali-metal acetates, the stronger bases (as determined potentiometrically) giving marked decreases on titration with perchloric acid, the weaker ones giving increases under the same conditions. As all the phosphazene bases described here are of approximately similar size, the change of behaviour must be related to increased electron density at the basic sites and this in turn will give rise to a greater concentration of free acetate ions capable of participating in the postulated proton-jump mechanism.

Experimental

Our earlier procedure[2] was somewhat modified.

Apparatus.—An Orion model 801 digital potentiometer, equipped with an Orion glass electrode and an Orion calomel electrode, was used. The calomel electrode was modified as follows: the aqueous saturated KCl solution was removed, the electrode was washed several times with anhydrous methanol to remove traces of moisture, and then filled with a saturated anhydrous methanol solution of KCl. A pressure of 20 mmHg was applied to this electrode to prevent diffusion into it of the titrating solution. A thin-tip semi-microburette was used, which enables the titrant solution to be read to 0.01 cm^3. The titration cell was a well shaped Jena 50-cm^3 beaker wound with thin copper wire, which was earthed. A magnetic stirrer, also earthed, was used. For the conductometric work an Orion Research conductivity meter model 101 was used. This meter and ancillary equipment were also earthed.

Chemicals.—Perchloric acid titrant was prepared as follows. Using a micropipette pure Merck 70% perchloric acid (0.72 cm^3) was added dropwise to pure acetic anhydride (5 cm^3) and cooled in ice to give a pale yellow solution (unless care was taken a vigorous reaction leading to a dark brown solution resulted). This pale yellow solution was allowed to stand at room temperature for 5—6 h. A portion (1 cm^3) of it was then introduced into a 50-cm^3 graduated flask and made up to 50 cm^3 with pure nitrobenzene (see below). The concentration of this solution was standardised against the primary standard, 1,3-diphenylguanidine, and found to be 0.034 mol dm^{-3}. This solution was used throughout this work. It was stable for 3—4 months, if kept in a dark flask in a refrigerator.

Nitrobenzene solvent was prepared as follows. To 1 l of pure Merck nitrobenzene was added 10 g of P_2O_5. The mixture was well shaken and then left to stand overnight. It was then distilled twice at 90 °C and 11 mmHg pressure, using an oil pump protected by a trap cooled with liquid air. The solvent thus prepared was straw coloured and had a refractive index of 1.5513.

Benzene, acetic anhydride, and acetic acid were pure Merck grade and used without further purification. The alkali-metal acetates were prepared from their carbonates *in situ* by dissolving them in acetic acid. The carbonates were obtained as follows: Li_2CO_3, Riedel De Haën AG (pure); Na_2CO_3, Merck 6 938 (wasserfrei reinst); K_2CO_3, Merck 4 924 (pure); Cs_2CO_3, Aldrich Chemical Co. Ltd. (pure, 99.9%); Rb_2CO_3, Aldrich (Gold Label).

Acknowledgements

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