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SOLVENT EFFECTS ON REACTIONS OF HYDROXIDE ION WITH PHOSPHORUS(V) ESTERS. A QUANTITATIVE TREATMENT

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Second-order rate constants of reactions of HO^- with phosphate, phosphinate and thiophosphinate esters, $(PhO)_2PO.OC_6H_4NO_2$-*p*, $Ph_2PO.OC_6H_4NO_2$-*p*, $Ph_2PO.SPh$, $Ph_2PO.SC_6H_4NO_2$-*p* and $Ph_2PO.SEt$, go through minima with decreasing water content of H_2O–MeCN or H_2O–*t*-BuOH. The rate decrease is due to stabilization of the non-ionic ester on addition of organic solvent to H_2O. This inhibition is partially offset by stabilization of the anionic transition states and in the drier solvents partial desolvation of HO^- increases rates.

INTRODUCTION

Solvent effects upon rates of reactions of nucleophilic anions are related to mechanism and Hughes and Ingold proposed a simple qualitative model for predicting these effects in terms of molecularity and charge type of S_N displacements at alkyl centers.[1] They predicted that a decrease in solvent polarity would mildly favor S_N2 reactions of anions, which involve dispersion of existing charge, and would strongly disfavor S_N1 reactions of non-ionic substrates where charge develops in the transition state. A decrease in anionic solvation in dipolar aprotic solvents markedly increases rates of S_N2 and *E*2 reactions, which makes solvents such as dimethyl sulfoxide useful as synthetic media and kinetic solvent effects upon S_N2 reactions have been treated quantitatively in terms of free energies of the anions, substrates and transition states in various solvents.[2,3]

A quantitative treatment of bimolecular ion–molecule reactions based on the effect of solvent dielectric constant, ε, on interactions of an ion with a dipole, predicts that log *k* should vary linearly with $1/\varepsilon$.[4] If the ionic radius of the transition state is larger than that of the ionic reactant rate constants should increase with decreasing dielectric constant in accord with the Hughes–Ingold rules.[1] This behavior is seen with S_N2 reactions in apolar solvents, but for some reactions rate constants decrease with decreasing dielectric constant, contradicting both the Hughes–Ingold rules and the quantitative treatment.[3] For example, for reaction of HO^- with methyl propionate in aqueous acetone, a plot of log *k* against $1/\varepsilon$ has a negative slope with curvature at low water content,[4] and added acetonitrile decreases rates of reactions of aqueous HO^- with phosphorus(V) esters.[5] The Hughes–Ingold rules and the quantitative electrostatic treatments have been discussed critically, especially as regards the concept of solvent polarity and the modelling of a solvent as a dielectric continuum.[3]

Rate constants of reactions in pure solvents can often be fitted to the solvatochromatic scale, which sets out to isolate the role of solvent properties such as electrophilicity, nucleophilicity, polarizability and cavity formation.[6] Other treatments focus on solvent nucleophilicity and ionizing power[7] or on donor–acceptor properties.[8] These treatments fit solvent effects for many reactions, although S_N reactions at alkyl centers are the most widely studied systems and they focus attention on the molecular-scale interactions that control kinetic solvent effects.

Nucleophilic attack is a potentially useful method for destroying toxic phosphorus(V) derivatives, e.g. phosphofluoridates.[9] Some of these compounds are sparingly soluble in water, or are mixed with water-insoluble polymeric thickeners, so it is necessary to use solubilizing agents, which may be organic solvents or association colloids, e.g. micelles or microemulsions.[5,9,10]

We have examined reactions of several (non-toxic) model compounds with HO^- (Scheme 1). These compounds are *p*-nitrophenyl diphenyl phosphate and phosphinate [$(PhO)_2PO.Ar$ and $Ph_2PO.OAr$, respectively], thioethyl and thiophenyl diphenyl phosphinate and *p*-nitrothiophenyl diphenyl phosphinate

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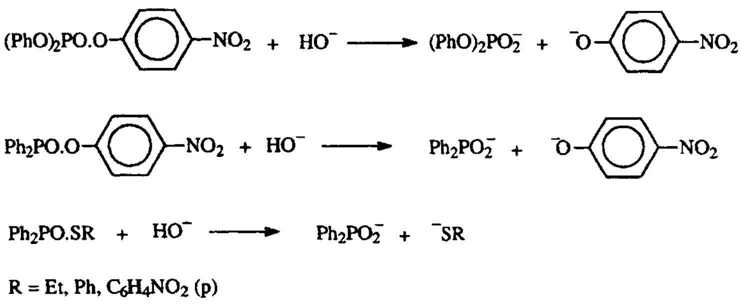


Scheme 1

($Ph_2PO.SEt$, $Ph_2PO.SPh$ and $Ph_2PO.SAr$ respectively: Ar denotes $C_6H_4NO_2$-*p*).

The *p*-nitrophenyl derivatives are convenient substrates because their reactions can easily be followed by monitoring formation of *p*-nitrophenoxide ion. We used either acetonitile (MeCN) or *tert*-butyl alcohol (*t*-BuOH) as organic solvents because they are unreactive towards the substrates and are miscible with aqueous electrolytes. They differ significantly in their polarities and dielectric constants.[11] Reactions of HO^- with phosphorus(V) esters are inhibited by initial addition of an organic solvent, e.g. MeCN,[5] which does not fit qualitative and quantitative treatments that are satisfactory for many reactions under these conditions.[1,3,4] It is reasonable to associate this inhibition with a decrease in the activity coefficient of the hydrophobic substrates on addition of organic solvent, so we determined activity coefficients of $(PhO)_2PO.OAr$, $Ph_2PO.OAr$, $Ph_2PO.SEt$ and $Ph_2PO.SPh$ in aqueous MeCN. Reactions of anionic nucleophiles and bases are typically very fast in aprotic solvents of low water content so rates[2,3] of reactions of these esters in these mixed solvents should go through minima with decreasing water content.

RESULTS AND DISCUSSION

Kinetics

Reactions with HO^- are overall second order. Second-order rate constants, k_2, in water are given in Tables 1–3. In agreement with earlier observations the phosphinate, $Ph_2PO.OAr$, is considerably more reactive than the phosphate, $(PhO)_2PO.OAr$, and the thioethyl derivative, $Ph_2PO.SEt$, is the least reactive substrate towards HO^-, consistent with the low leaving group ability of EtS^-, relative to $O_2NC_6H_4O^-$ or $O_2NC_6H_4S^-$.[5,12–14] Second-order rate constants in the more aqueous solvents agree with earlier values,[5] and the reactivity sequence in water is $Ph_2PO.SAr > Ph_2PO.OAr > Ph_2PO.SPh > (PhO)_2PO.OAr > Ph_2PO.SEt$.

Table 1. Second order rate constants of reactions of the *p*-nitrophenyl derivatives and substrate activity coefficients[a]

		Ester				
		$(PhO)_2PO.OC_6H_4NO_2$		$Ph_2PO.OC_6H_4NO_2$		$Ph_2PO.SC_6H_4NO_2$
MecN (vol.%)	χ_{MeCN}	k_2	γ_s	k_2	λ_s	k_2
0		0·52[b]	1·00	18·6[b]	1·00	23·5[b]
0·4				18·3 (0·98)	0·96	21·2 (0·90)
2·12	0·0074	0·458 (0·88)				
10·4	0·038	0·304 (0·58)	0·159	14·4 (0·77)	0·263	19·5 (0·83)
20·3	0·081	0·198 (0·38)	0·025	9·51 (0·51)	0·073	15·3 (0·65)
40·2	0·189	0·081 (0·16)	$6{\cdot}9 \times 10^{-4}$	5·17 (0·28)	$5{\cdot}8 \times 10^{-3}$	10·8 (0·46)
60·2	0·343	0·064 (0·12)	$5{\cdot}2 \times 10^{-5}$	4·66 (0·25)	$6{\cdot}3 \times 10^{-4}$	9·54 (0·41)
80·1	0·582	0·162 (0·31)		9·86 (0·53)		21·5 (0·91)
84·1	0·646	0·231 (0·44)		14·0 (0·75)[c]		29·2(1·24)

[a] Second order rate constants, $M^{-1}\ s^{-1}$, at 25.0 °C in H_2O–MeCN; values of k_2/k_2^0 are in parentheses; values of γ_s were interpolated where necessary.
[b] Extrapolated values.
[c] Values obtained with Bu_4NOH or NaOH agreed.

Table 2. Second order rate constants of reactions of thiol phosphinates and substrate activity coefficients[a]

MecN (vol.%)	χ_{MeCN}	Ester $Ph_2PO.SEt$ k_2	 γ_s	 $Ph_2PO.SPh$ k_2	 λ_s
0		0·277[b]	1·00	2·49[b]	1·00
1·0	0·0035	0·263 (0·95)	0·91	2·32 (0·93)	0·88
2·5	0·0088	0·247 (0·89)	0·79	2·18 (0·88)	0·72
5·0	0·018	0·222 (0·80)	0·62	1·89 (0·76)	0·52
10·0	0·037	0·185 (0·67)	0·38	1·56 (0·63)	0·28
15·0	0·058			1·28 (0·51)	0·14
20·0	0·08	0·113 (0·41)	0·15	1·08 (0·43)	0·076
40·0	0·188	0·064 (0·23)	0·021	0·527 (0·21)	$5·7 \times 10^{-3}$
55·0	0·297	0·053 (0·19)	$6·3 \times 10^{-3}$		
60·0	0·342			0·560 (0·22)	$5·7 \times 10^{-4}$
70·0	0·447	0·074 (0·27)			
75·0	0·509			0·647 (0·26)	
85·0	0·662	0·173 (0·62)		1·32 (0·53)	

[a] Second-order rate constants, $M^{-1} s^{-1}$, at 25.0 °C in H_2OMeCN; values of k_2/k_2^0 are in parentheses; rate constants on 0–20 vol.% MeCN are from Ref. 5.
[b] Extrapolated values.

Table 3. Second order rate constants in H_2O–*t*-BuOH[a]

t-BuOH (wt%)	χ_{BuOH}	Ester $(PhO)_2PO.OC_6H_4NO_2$	 $Ph_2PO.OC_6H_4NO_2$	 $Ph_2PO.SEt$	 $Ph_2PO.SC_6H_4NO_2$
0		0·52[b]	18·6[b]	0·277[b]	23·5[b]
16·5	0·046		6·76 (0·36)		11·4 (0·49)
20·2	0·058	0·091 (0·18)		0·052 (0·19)	
32·0	0·103	0·050 (0·10)	5·60 (0·30)	0·036 (0·13)	7·80 (0·33)
56·9	0·243	0·073 (0·14)	6·76 (0·36)	0·066 (0·24)	10·4 (0·44)
75·1	0·423	0·185 (0·36)			21·4 (0·91)
84·4	0·568	0·285 (0·55)	16·6 (0·89)[c]	0·19 (0·70)	

[a] Values of k_2, $M^{-1} s^{-1}$, at 25.0 °C in H_2O–*t*-BuOH; values of k_2/k_2^0 are in parentheses.
[b] Extrapolated values.
[c] The same value was obtained with Bu_4NOH instead of NaOH.

Structural effects on the rates of these reactions have been discussed in detail.[5,12–14]

Kinetic solvent effects

The dependence of k_2 on solvent composition at 25·0 °C is illustrated in Tables 1–3, with values of k_2/k_2^0, where k_2^0 is the second order-rate constant in water. Qualitatively all these kinetic solvent effects are similar, although values of k_2/k_2^0 in a given solvent differ considerably for some substrates.

Comparison of the dependence of k_2/k_2^0 on the mole fraction of the organic solvent shows that the very different polarities of MeCN and *t*-BuOH[10] do not control their kinetic effects. For example, the dielectric constant of MeCN is 35·9 and the linear cyano group has a strong dipole moment, whereas *t*-BuOH has a low dielectric constant (12·5) and is approximately spherical. Therefore, molecular interactions of water with reactants and the transition state seem to be a major factor in determining the dependence of rate on solvent composition over the range that we examined. However, the mole fraction of organic solvent at the rate minima is lower with *t*-BuOH than with MeCN (Tables 1–3).

Activity coefficients of the esters

Activity coefficients, γ_s, of $(PhO)_2PO.OAr$, $Ph_2PO.OAr$, $Ph_2PO.SPh$ and $Ph_2PO.SEt$ were determined in H_2O–MeCN by partitioning them between the aqueous medium and pentane (Tables 4 and 5). The measurements were not made in H_2O–*t*-BuOH because this alcohol is readily soluble in pentane, or with

Table 4. Activity coefficients of $Ph_2PO.OAr$

MeCN (vol.%)	Extracted (%)	Log γ_s[a]
0.8	87	−0·08 (0.00)
3.0	69	−0.24
10.0	83	−0.61 (−0.64)
20.0	35	−1.17 (−1.18)
20.0	58	−1.15
30.0	83	−1.62 (−1.84)
40	53	−2.25 (−2.27)
70.0	16	−3.64

[a] Calculated from absorbance of *p*-nitrophenoxide ion (402 nm); values in parentheses are calculated from absorbance of unreacted ester.

Table 5. Activity coefficients of $(PhO)_2PO.OAr$, $Ph_2PO.SPh$ and $Ph_2PO.SEt$[a]

MeCN (vol.%)	$(PhO)_2PO.OAr$[b]	$Ph_2PO.SPh$	$Ph_2PO.SEt$
0·8		−0·02	
2·8			−0·06
5·0			−0·29
5·7	−0·42		
10·0	−0·76	−0·54	−0·40
20·0	−1·54	−1·16	−0·84[c]
30·0	−2·32		−1·24
40·0	−3·10 (−3·08)	−2·23	−1·64
55·0			−2·20
60·0	−4·26	−3·24	

[a] Values of log γ_s calculated from absorbance of the ester, unless specified otherwise, with a solution in water as the standard state.
[b] Calculated from absorbance of *p*-nitrophenoxide ion (402 nm); the value in parentheses is calculated from absorbance of the ester.
[c] With 42% extraction, with more pentane and 65% extraction log $\gamma_s = -0.85$.

$Ph_2PO.SAr$ because its hydrolysis is inconveniently rapid even when reaction with HO^- is suppressed by dilute acid. Experiments were not made in the solvents of low water content because MeCN is partially extracted into pentane at >60 vol.% MeCN.

Values of γ_s decrease sharply on addition of MeCN to H_2O and plots of log γ_s against vol.% MeCN, or the mole fraction of MeCN, χ_{MeCN}, are linear, except in the least aqueous solvent, and fit the equation

$$\log \gamma_s = -K_s\chi_{MeCN} \tag{1}$$

with $K_s = -16{\cdot}3$ and $-11{\cdot}8$ for $(PhO)_2PO.OAr$ and $Ph_2PO.OAr$, respectively, and for the thio compounds $K_s = -11{\cdot}8$ and $-8{\cdot}8$ for $Ph_2PO.SPh$ and $Ph_2PO.SEt$, respectively.

Treatment of kinetic solvent effects

Decreases in activity coefficients of the substrates are responsible for the rate decreases on addition of MeCN to H_2O (Tables 1–3). Application of the Brønsted–Bjerrum rate equation gives[3]

$$k_2/(k_2^0\gamma_s) = \gamma_{OH}/\gamma_* \tag{2}$$

where k_2^0 is the second-order rate constant in water, which is taken as the standard state, and γ_{OH} and γ_* are activity coefficients of HO^- and the transition state, respectively.

Plots of $\log(\gamma_{OH}/\gamma_*)$ against vol.% MeCN are linear (Figure 1). Slopes decrease in the sequence $(PhO)_2PO.OAr > Ph_2PO.OAr \approx Ph_2PO.SPh > Ph_2PO.SEt$. They are measures of $\log \gamma_{OH}/\gamma_*$, and we cannot separate these terms, but from the slopes we estimate relative values of $\log \gamma_*$. Relative to γ_* for reaction of $(PhO)_2PO.OAr$ (the reference compound), $\gamma_*(Ph_2PO.OAr) \approx \gamma_*(Ph_2PO.SPh) \approx 1.3$ and $\gamma_*(Ph_2PO.SEt) \approx 2.1$, over the range 0–60 vol.% MeCN.

The transition states are bulky, charge-delocalized monoanions and the substrates are bulky neutral molecules, so from the point of view of size their interactions with solvents should be similar and γ_s and γ_* should be related. Plots of $\log(\gamma_{OH5}\gamma_*)$ against $\log \gamma_s$ are linear, with a slight upward curvature, and for the *p*-nitrophenyl and thiophenyl substrates the plots are almost coincident and slopes, a, are $-0{\cdot}75$. For $Ph_2PO.SEt$ $a = -0{\cdot}65$ (Figure 2). The relationship between $\log(\gamma_{OH}/\gamma_*)$ and $\log \gamma_s$ is, in 0–60 vol.% MeCN

$$\log(\gamma_{OH}/\gamma_*) = a \log \gamma_s \tag{3}$$

but

$$\log(k_2/k_2^0) = \log \gamma_s + \log(\gamma_{OH}/\gamma_*) \tag{4}$$

$$= (1 + a)\log \gamma_s \tag{5}$$

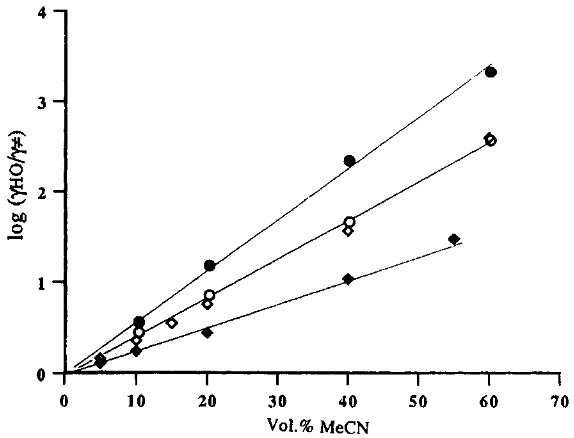


Figure 1. Dependence of $\log(\gamma_{OH}/\gamma_*)$ on solvent composition for reactions with HO^- in H_2O–MeCN. ●, $(PhO)_2PO.OAr$; ○, $Ph_2PO.OAr$; ◇, $Ph_2PO.SPh$; ◆, $Ph_2PO.SEt$

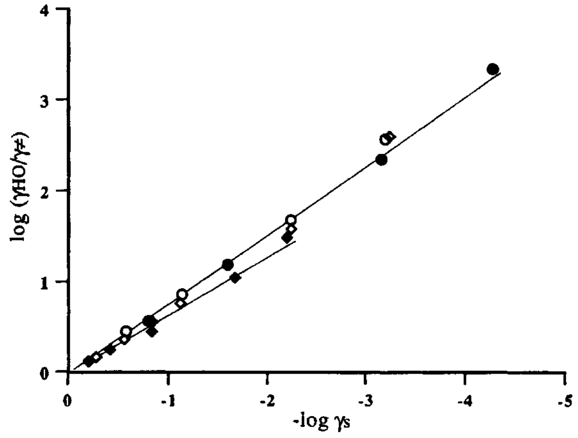


Figure 2. Relationships between $\log(\gamma_{OH}/\gamma_{\neq})$ and $\log \gamma_s$ for reactions with HO^- in H_2O–MeCN. Symbols as in Figure 1.

For the nitrophenyl and thiophenyl substrates $(1 + a) = 0{\cdot}25$ and

$$\log(k_2/k_2^0) = 0{\cdot}25 \log \gamma_s = -0{\cdot}33 \log(\gamma_{OH}/\gamma_{\neq}) \quad (6)$$

For the thioethyl substrate $(1 + a) = 0{\cdot}35$ and

$$\log(k_2/k_2^0) = 0{\cdot}35 \log \gamma_s = -0{\cdot}54 \log(\gamma_{OH}/\gamma_{\neq}) \quad (7)$$

The similar absolute values, and opposite signs, of the coefficients in equations (6) and (7) are readily understandable. A decrease in the water content of aqueous MeCN decreases γ_s (Tables 1 and 2), i.e. it lowers the free energy of the substrate, but this inhibition is partially offset by stabilization of the bulky, monoanionic transition state, i.e. by a decrease in $\gamma_{\neq}$. There should also be a rate-enhancing effect due to an increase in γ_{OH}, but it seems to be relatively unimportant in the range of 0–60 vol.% MeCN, probably because even in 60 vol.% MeCN $\chi_{H_2O} \approx 0{\cdot}65$ and HO^- should still be strongly hydrated.

The increases in values of $\log(\gamma_{OH}/\gamma_{\neq})$ on addition of MeCN to water, as shown by the slopes of plots in Figure 2 [equation (2)] are consistent with qualitative and quantitative predictions of solvent effects on bimolecular ion–molecule reactions based on the relative solvation energies of high and low charge-density ions.[1-3] If the transition state is a very large, low charge-density ion as in our reactions, it will be stabilized, i.e. its activity coefficient will decrease, on addition of an organic solvent to water. The consequent rate enhancement will be offset by the decrease in γ_s (substrate stabilization), which may generate the rate minima because in the drier solvent γ_{OH} increases by desolvation of HO^-.[1-3] This analysis neglects interactions of the cations (Na^+ or Bu_4N^+) in the initial and transition states but rate constants are independent of the nature of the cation (Tables 1 and 3). However, in some reactions these interactions are very important.[15]

The rate minima with decreasing water content in both H_2O–MeCN and H_2O–*t*-BuOH show that stabilization of the non-ionic substrates is initially greater than that of the corresponding transition state where charge is dispersed over oxygen or sulfur centers, cf. equations (3)–(7), because γ_{OH} does not decrease on addition of the organic solvents.

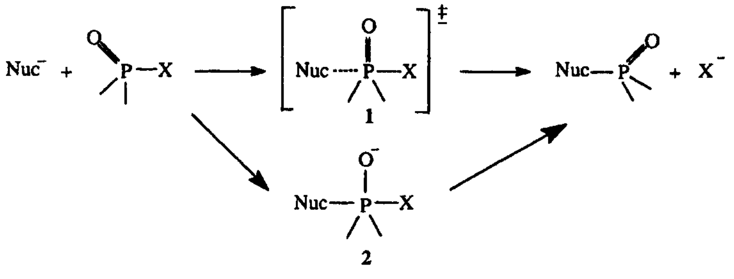
There is the possibility that structures of initial and transition states will be such that interactions with solvent are the same in the two states and activity coefficients will then cancel, i.e. $\gamma_s\gamma_{OH}/\gamma_{\neq} = 1$, and rate constants will be solvent independent. This possibility was considered by Zucker and Hammett[16] in their original discussion of relationships between rates of acid-catalyzed hydrolyses and acidity, although it does not apply to the present reactions of HO^-.

Our general conclusions are consistent with the values of *a* [equation (3)] from slopes of plots of log $(\gamma_{OH}/\gamma_{\neq})$ against $\log \gamma_s$, i.e. the factors that control stabilization of the substrates by addition of MeCN apply also to the transition states, although the effects are somewhat attenuated (i.e. slopes are *ca* $-0{\cdot}7$, Figure 2).

These comparisons indicate that transition states for reactions of the four substrates with HO^- do not differ strongly in the development of charge or its distribution, despite differences in the aryloxide and thiolate leaving groups. For example, hydrogen bonding should be stronger towards an oxide as compared with a thiolate ion,[3,17] so we believe that bond breaking is not very extensive in the transition state. This conclusion is consistent with observations that although electron withdrawing substituents in the leaving phenoxy groups speed reaction, the effect is much less than upon acidities of the phenols.[5,12-14] This comparison is especially evident for reactions of $Ph_2PO.SAr$ and $Ph_2PO.SPh$ (Tables 1 and 3).

Reactions of nucleophiles with phosphorus (V) esters can be stepwise or concerted.[12-14,18] Scheme 2 shows transition state **1** for a concerted reaction with charge only on the entering and leaving groups, as assumed for an S_N2 reaction at a primary alkyl center.[1] For such a transition state the Hughes–Ingold rules and quantitative treatments predict that rates should increase with decreasing water content of the solvent.[1,3,4] However, charge is probably also dispersed into the P=O residue and in that event it is difficult to make a distinction between a concerted reaction and a stepwise reaction with a very short-lived intermediate (**2**). However, the weak correlation of rates and stabilities of the leaving anions,[5,12-14] as given by the acid dissociation constants, and applications of the Hammond postulate, or similar free energy models,[19] indicate that bond-breaking is not extensive in the transition states.

We could not estimate γ_s in H_2O–*t*-BuOH, or for



Scheme 2

$Ph_2PO.SAr$, but dependence of k_2/k_2^0 on solvent composition is similar for all reactions with HO^- (Tables 1–3), so we assume that our general conclusions apply under all the conditions that we used.

Except in the driest solvents, rates are governed largely by medium effects on the relative free energies of the esters and transition states, rather than by destabilization of HO^-, and stabilization of the esters by the organic solvents is partially offset by stabilization of the transition states. In solvents of very low water content, hydration of HO^- decreases, i.e. γ_{OH} increases sharply. We cannot test this point experimentally but, if we assume that plots of γ_s against vol.% MeCN or χ_{MeCN} will continue to be linear with MeCN > 60 vol.%, and calculate γ_s by using equation (1), plots of $\log(\gamma_{OH}/\gamma_{\ast})$ against vol.% MeCN (Figure 1) or against $-\log \gamma_s$ (Figure 2) would curve sharply upwards. Such a deviation from linearity is expected if γ_{OH} increases in the drier solvents.

CONCLUSIONS

Comparison of kinetic solvent effects with activity coefficients of the substrates in aqueous MeCN shows that the typical inhibition due to decreasing water content of the solvent (Tables 1–3) is largely due to stabilization of the substrate by the organic solvent, which initially overcomes the rate enhancement due to destabilization of the anionic nucleophile relative to the transition state. Destabilization of the nucleophile becomes the dominating factor in the rate enhancements in the less aqueous solvents.[1-3] A decrease in the water content of the solvent decreases the activity coefficients of the substrates, γ_s, but this inhibition is partially offset by an increase in $\gamma_{OH}/\gamma_{\ast}$. However, the linear relationships between $\log \gamma_s$ and $\log(\gamma_{OH}/\gamma_s)$ or between $\log k_2$ and $\log \gamma_s$ [equations (3)–(7) and Figures 1 and 2] indicate that an increase in γ_{OH} is not of major importance in <60 vol.% MeCN, where there is ample H_2O for hydration of HO^-.

We cannot treat some reactions quantitatively; however, the similarity of the kinetic solvent effects in aqueous *t*-BuOH with those in aqueous MeCN (Tables 1 and 3) indicates that similar factors are involved in the two systems. The lower polarity and dielectric constant of *t*-BuOH as compared with MeCN[10] seems to be relatively unimportant, indicating that the controlling factor is hydration of reactants and the transition state.

The partial compensation between solvent effects upon γ_s and $\gamma_{\ast}$ which leads to the rate minima in plots of k_2/k_2^0 against solvent composition (Tables 1–3) does not apply to all ion–molecule reactions. Solvent effects in S_N2 reactions of anions at alkyl centers are as predicted in terms of solvation energies of small and large (charge-dispersed) anions.[1-4] These reactions differ from those of esters where charge in the transition state may be on electronegative oxygen centers. Both the Hughes–Ingold rules[1] and the electrostatic treatments[3,4] focus attention on interactions of solvents with ions or ion pairs, and do not explicitly consider interactions with non-ionic solutes.

EXPERIMENTAL

Materials. Most of the esters were samples used earlier.[5] The sample of $Ph_2PO.SC_6H_4NO_2$-*p* was prepared by the method of Bourne *et al.*[18a] and was recrystallized twice from 2-propanol. It had m.p. 149–151 °C. A previously prepared sample with m.p. 121–123 °C had been described as containing impurities.[12c] Our sample gave a single spot on TLC (1:1 hexane–ethyl acetate) and examination of its ^1H NMR spectrum in $CDCl_3$ showed that it was not contaminated by the thiol or phosphinic acid. Kinetic solutions were made by volume (H_2O–MeCN) or by weight (H_2O–*t*-BuOH), with *t*-BuOH distilled over Na. Redistilled CO_2-free water was used for the kinetics.

Kinetics. Reactions were followed spectrophotometrically at 25·0 °C in Hewlett-Packard diode-array spectrophotometers, with [substrate] = $(1-4) \times 10^{-5}$ M.[5] Most experiments were made with NaOH, but occasionally we used Bu_4NOH (Tables 1 and 3). Generally $[OH^-]$ = 1–30 mM and plots of first-order rate constants against $[HO^-]$ were linear with zero intercept. Reactions were followed at 400–430 nm for esters with

$O_2NC_6H_4O^-$ and $O_2NC_6H_4S^-$ leaving groups, 264 nm for $Ph_2PO.SPh$ and 245–250 nm for $Ph_2PO.SEt$, as described.[5] Some of the reactions had been followed earlier and our current rate constants agree with earlier values;[5] for example, for the reaction of $Ph_2PO.SEt$ in 20 vol.% MeCN at 0.03 M KOH, k_{obs} was $3{\cdot}4 \times 10^{-3}\ s^{-1}$, which is the earlier value.[11]

Activity coefficients. Substrates were partitioned between pentane and aqueous MeCN.[20] Solutions of $(PhO)_2PO.OAr$, $Ph_2PO.OAr$, $Ph_2PO.SPh$ and $Ph_2PO.SEt$ in aqueous MeCN were extracted into pentane and concentrations of unextracted esters in the aqueous layer were calculated spectrophotometrically either from absorbances of the esters at 268, 273, 264 and 223 nm for $(PhO)_2PO.OAr$, $Ph_2PO.OAr$, $Ph_2PO.SPh$ and $Ph_2PO.SEt$, respectively, or at 402 nm for the *p*-nitrophenoxy derivatives after reaction with HO^-. Volumes of pentane and aqueous MeCN were adjusted so that between 15 and 87% of the ester was extracted. An example of the procedure is given for $Ph_2PO.OAr$ in Table 4, and data for the other esters are given in Table 5. Aqueous solutions contained *ca* 10^{-4} M HCl to suppress reaction of $Ph_2PO.SPh$ with adventitious base. Values of γ_s in Tables 1 and 2 were obtained by interpolation where necessary, and are referred to dilute aqueous solutions as the standard state.

Additional specific data on rates and transfer equilibria are available from the authors.

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