Solvolysis Rates of Diarylmethyl *p*-Nitrobenzoates in Aqueous Ethanol. The Question of Solvent Assistance and the Validity of Selectivity Probes

By **Duncan J. McLennan** * and **Peter L. Martin**, Department of Chemistry, University of Auckland, Auckland, New Zealand

Rate constants for solvolysis of diarylmethyl *p*-nitrobenzoates in ethanol–water and trifluoroethanol–water mixtures have been measured. Hammett ρ values and Winstein–Grunwald *m* parameters have been evaluated. The former are insensitive to solvent composition and the latter to ring substituent. Mechanistic speculation is required before these results can be assessed as contributors to debate on the reactivity–selectivity principle, and it is concluded, on the basis of the trifluoroethanol–water probe, that solvent assistance is absent.

THIS and the following paper bring together our interest in mechanisms of nucleophilic aliphatic substitution reactions and in the contentious status of the reactivity–selectivity principle (RSP).

The RSP has received detailed and critical re-evaluation in recent years [1-14] and a good proportion of studies have used S_N reactions as probe processes.[6-14] There are two aspects to the principle. The *practical* expectation is that high reactivity should be associated with low selectivity and *vice versa*. A *conceptual* corollary, loosely and often incorrectly based on the Hammond postulate, is that transition states of unselective reactions should resemble reactants in structure and energy whilst those of selective reactions should resemble products. The one certain picture emerging from the plethora of studies on the RSP and its consequences is one of inconsistency and confusion.

Part of the confusion may lie in the possibility that the measured selectivity parameters may or may not always be indices of transition state (TS) character. A second problem is that the probe reactions do not always have well understood mechanisms, so there is no certainty that an experimentally determined selectivity parameter is in fact providing the required information. Furthermore, different experimental approaches can yield conflicting conclusions (see refs. 6, 14, and 15 for an example of conflicting views on Menschutkin reactions). A final source of uncertainty is that once the simple Hammond postulate approach is replaced by a more realistic approach based on reactants, products, and potential intermediates,[16] it becomes possible to reconcile constant selectivity with TS variation [1,4,11,12] (hardly of interest as far as the practical consequences of the RSP are concerned). Unfortunately, it also becomes possible to rationalize almost any response of reactivity to substituent or reagent change by judicious choice of the co-ordinates of the initial unperturbed TS on the potential energy surface.

Refs. 6—14 exemplify cases where the RSP has been probed *via* S_N reactions. Yet reactions in this class have been the subject of intense mechanistic debate, especially in the past decade. In view of uncertainty associated with detailed mechanistic features of bimolecular [17] and solvolytic [18,19] processes it is little wonder that contradictory interpretations concerning the RSP have emerged.

In the present work we attempt to use selectivity probes to address several questions. To what extent does a nucleophile or nucleophilic solvent molecule assist carbon-leaving group heterolysis, and how widespread is such assistance? Are ionic intermediates obligatory, whether formed with assistance or not, or are concerted pathways enforced under certain circumstances? [19b] How reliable are selectivity parameters in providing answers to such questions? Some of the results considered here have been reported elsewhere in another context; [20] they are now amplified and analysed in an attempt to unravel mechanistic details. We have previously suggested that the solvolysis of diphenylmethyl *p*-nitrobenzoate in acetone–ethanol–water mixtures may involve a solvent assistance component [21] and we subject this point to closer scrutiny.

RESULTS

Rate constants for the solvolysis of diarylmethyl *p*-nitrobenzoates, (p-RC_6H_4)(p-$R'C_6H_4$)CHOPNB, in solvent mixtures ranging from 80% (v/v) ethanol–water (80E) to 50% ethanol–water (50E) at 100 °C have already been recorded,[20] as have data for Ph_2CHODNB (ODNB = 3,5-dinitrobenzoate). The temperature dependence of the rate constants for solvolysis of (p-MeC_6H_4)$_2$CHOPNB in the ethanol–water solvents is shown in Table 1. Rate constants in Table 2 pertain to the solvolysis of Ph_2CHOPNB in

TABLE 1

Rate constants as a function of temperature for the solvolysis of (p-MeC_6H_4)$_2$CHOPNB in ethanol–water mixtures

Solvent	$10^5k/s^{-1}$						
	25 °C [a]	50 °C	60 °C	70 °C	100 °C [a]	$\Delta H^‡$ [b]	$\Delta S^‡$ [c]
80E	0.118	2.76	8.57	24.7	412 [d]	23.3	−7.4
70E	0.235	5.95	18.8	56.2	1 010	23.9	−4.2
60E	0.531	12.0	39.0	106	1 780	23.1	−5.0
50E	0.874	21.8	67.4	203	3 560	23.7	−2.1

[a] Extrapolated. [b] In kcal mol^{-1}. [c] In cal K^{-1} mol^{-1}. [d] Experimental measurement yielded a rate constant, k 417 × 10^{-5} s^{-1}.

TABLE 2

Solvolysis rate constants for $Ph_2CHOPNB$ in CF_3-CH_2OH–H_2O solvent mixtures (w/w) at 100 °C

Solvent[a]	100T	97T	80T	70T
$10^5k/s^{-1}$	112	102 ± 1	122 ± 2	136 ± 5

[a] *E.g.* 97T = 97% TFE–3% H_2O (w/w).

TABLE 3

Molar solubilities[a] of substituted diphenylmethyl *p*-nitrobenzoates in ethanol–water solvents at 25 °C

	Solvent			
Ester	80E	70E	60E	50E
$(p\text{-}MeC_6H_4)_2CHOPNB$	13.6	3.81	1.91	0.384
$Ph_2CHOPNB$	16.4	6.90	2.51	0.743
$(p\text{-}ClC_6H_4)_2CHOPNB$	8.64	3.35	0.880	0.200

[a] Ester concentration in a saturated solution, expressed as 10^4[ester] in units of mol l^{-1}.

trifluoroethanol–water solvent mixtures at 100 °C. The molar solubilities of selected diarylmethyl *p*-nitrobenzoates in ethanol–water solvent mixtures are shown in Table 3.

There are various ways of analysing these results, and the following Tables contain derived parameters. Plots of log*k* *versus* $\Sigma\sigma^+$ [22] for solvolysis of the substituted esters in each ethanol–water solvent yield linear Hammett plots, and the ρ values are shown in Table 4. Rate constants for $(p\text{-}ClC_6H_4)_2CHOPNB$ lay slightly above the plots described by the other points; the deviations expressed in log*k* units as Δ_{Cl} are also shown. Plots of log*k* *versus* the Winstein–Grunwald *y* parameters (Bu^tCl scale) [23] for solvolysis of a given ester in the series of solvents yields the m_{WG} parameters shown in Table 5. Also displayed are m_{OTs} values which are based on the y_{OTs} scale determined by solvolysis rates of 2-adamantyl tosylate in various solvents.[24] The solvent sensitivity of rates can be correlated in two other ways. The two-parameter equation (1) expresses solvent sensitivity in terms of a blending parameter *Q* which is a measure of a systems likeness to MeOTs or 2-AdOTs behaviour. The four-parameter expression (2) introduces explicit solvent

$$\log(k/k_0) = (1 - Q)\log(k/k_0)_{MeOTs} + Q\log(k/k_0)_{2\text{-}AdOTs} \quad (1)$$

polarity (*Y*) and nucleophilicity (*N*) terms based on the respective behaviour of 2-adamantyl tosylate and methyl tosylate.[24] Results of correlations are shown in Table 6.

$$\log(k/k_0)_{ROPNB} = mY + lN \quad (2)$$

Although equations (1) and (2) properly apply only to solvolysis of tosylates, the departing *p*-nitrobenzoate group is not sufficiently different in nature from the toluene-*p*-sulphonate group to cause serious concern.

TABLE 4

Hammett equation analysis of ester solvolysis in ethanol–water solvents at 100 °C

Solvent	ρ[a]	*r*[b]	Δ_{Cl}
80E	-3.18 ± 0.10	0.998	0.093
70E	-3.19 ± 0.10	0.998	0.082
60E	-3.13 ± 0.08	0.999	0.041
50E	-3.11 ± 0.05	0.999	0.039

[a] Uncertainties are standard deviations of slopes. [b] Correlation coefficient.

TABLE 5

Winstein–Grunwald equation analysis of solvolysis of $(p\text{-}RC_6H_4)(p\text{-}R'C_6H_4)CHOPNB$ in ethanol–water solvents at 100 °C

R	R′	m_{WG}[a]	*r*[b]	m_{OTs}[a]	*r*[b]
Me	Me	0.55 ± 0.02	0.998	0.70 ± 0.02	0.999
Me	H	0.56 ± 0.01	0.999	0.71 ± 0.01	0.999
H	H	0.62 ± 0.01	0.999	0.79 ± 0.01	0.999
Cl	H	0.60 ± 0.02	0.998	0.76 ± 0.02	0.999
Br	H	0.60 ± 0.01	0.999	0.77 ± 0.02	0.998
Cl	Cl	0.56 ± 0.01	0.999	0.71 ± 0.01	0.999
H	H[c]	0.52 ± 0.02	0.998	0.66 ± 0.02	0.998

[a] Uncertainties are standard deviations of slopes. [b] Correlation coefficient. [c] 3,5-Dinitrobenzoate ester.

TABLE 6

Extended correlations of solvolysis rates of $(p\text{-}RC_6H_4)$-$(p\text{-}R'C_6H_4)CHOPNB$ in ethanol–water solvents at 100 °C

R	R′	*Q*	*l*	*m*
Me	Me	0.63	0.37	0.74
Me	H	0.64	0.36	0.75
H	H	0.68	0.32	0.78
Cl	H	0.67	0.34	0.76
Br	H	0.66	0.34	0.75
Cl	Cl	0.64	0.36	0.75
H	H[a]	0.59	0.41	0.71

[a] 3,5-Dinitrobenzoate ester.

DISCUSSION

ρ *and* m *as Mechanistic Probes*—The ρ values in Table 4 and the m_{WG} parameters in Table 5 are not independent data sets.[25] The fact that ρ for the *p*-nitrobenzoates is essentially invariant with respect to solvent change ensures that m_{WG} will likewise be similar for all substituted esters. The fact that m_{WG} is lower for the 3,5-dinitrobenzoate probably has no mechanistic significance; more extensive delocalization of the incipient negative charge in the transition state is possibly the reason for this.[26] The m_{WG} value for diphenylmethyl chloride (0.74) [23] is indeed larger than the average value for the esters.

It can be predicted that the response of m_{WG} to substituent variation will be different for cases where nucleophilic assistance to substrate ionization is important as opposed to cases where unassisted ionization is the rate-limiting step.[13] Use of this probe, allied with secondary α-deuterium isotope effect studies, leads to the suggestion that solvent assistance, possibly *via* an S_N2 (intermediate) [24,27] or Doering–Zeiss [28] mechanism, is of importance in the solvolysis of substituted diphenylmethyl chlorides (m_{WG} decreases as σ^+ increases).[13] On the other hand the solvolyses of compounds in the $Bu^t_2ArCOPNB$ series are characterized by increasing m_{WG} with increasing σ^+ (a classical RSP result),[29] and an S_N1 ionization mechanism is thereby indicated.

In these terms the present finding of an essentially invariant m_{WG} value with substituent variation is singularly uninformative with respect to mechanism. It is now necessary to enquire as to whether *m* is even a measure of TS polarity relative to the polarity of the Bu^tCl or 2-adamantyl tosylate transition states, as is usually implicitly assumed, or not.

Abraham and his co-workers have most cogently pointed out that the act of substrate ionization in solution must be accompanied by creation of a solvent cavity, necessarily different in size and shape from the cavity accommodating the initial state, before the solvent can electrostatically stabilize the polar TS.[30-32]

Thus in calculating free energies of transfer of transition states from a standard solvent to a solvent system of interest by considering $\delta\Delta G^\ddagger$, the solvent effect on the observed free energy of activation, and ΔG_t°, the free energy of transfer of the initial state solute, *via* equation (3), one must be certain to correct for the cavity or size

$$\Delta G_t^\circ\ (\mathrm{TS}) = \delta\Delta G^\ddagger + \Delta G_t^\circ \qquad (3)$$

effect in some way so as to isolate the electrostatic contribution to the free energy of transfer of the transition state. Abraham[30] has estimated ΔG_E, the electrostatic contribution, for a variety of solvolysis transition states, and by comparing the values with those for a model ion pair has been able to evaluate charge separations, Z, for the transition states of these solvolyses. Some sample results are shown in Table 7, together with m_WG values for solvolysis in methanol–water mixtures.[33] It can be clearly seen that a correspondence between Z and m_WG exists. At first sight this may be surprising; in all cases initial state destabilization rather than transition state stabilization dominates the rate increase induced by changing the solvent from methanol to water. This is not specific to methanol and water; the same situation is found for ethanol–water mixtures.[34,35] However, for $\mathrm{Pr^iBr}$ for example where ΔG_t° (TS) *ca.* 0, the negative value of $\Delta G_\mathrm{E}^\circ(\mathrm{TS})$, the electrostatic (or internal)[32] component of $\Delta G_t^\circ(\mathrm{TS})$, must therefore be almost exactly cancelled by a positive $\Delta G_\mathrm{cav}^\circ$ (TS) term (the work required to create a solvent cavity for the TS) as the solvent is changed from ethanol to water. The latter is comprehensible in terms of the differing structures of the two liquids, but tells us little about the intrinsic size of the transition state.

TABLE 7

Parameters pertaining to solvolysis of various solutes in methanol–water mixtures

Solute	ΔG_t° [a]	ΔG_t° (TS) [b]	Z	m_WG
$\mathrm{Bu^tCl}$	4.09	−2.13	0.85	1.00 [c]
$\mathrm{Bu^tBr}$	4.07	−1.86	0.82	0.94
$\mathrm{Bu^tI}$	4.27	−1.31	0.77	0.89
$\mathrm{Pr^iBr}$	3.3	−0.3	0.51	0.54 [c,d]
$\mathrm{PhCH_2Cl}$	4.54	1.40	0.40	0.39 [c]
BuBr	3.9	2.1	0.27	0.32 [c]
MeI	1.90	0.06	0.31	0.29 [c]

[a] Free energy of transfer (molar scale) of solute from methanol to water in kcal mol^{-1}. [b] Same for solvolysis transition state. [c] Based on methanol–water data. [d] Ref. 32.

Although calculations of this type are not currently possible for substrates as complex as those considered here, we can at least go part of the way by dissecting solvent effects into initial state and transition state contributions in an attempt to see whether $\mathrm{Ar_2CHOPNB}$ solvolyses fit into established patterns. The solvent structure effect mentioned above was considered to be of lesser importance since mixed solvents of a narrow composition range were being considered.

An exact dissection is possible for the solvolysis of $(p\text{-}\mathrm{MeC_6H_4})_2\mathrm{CHOPNB}$, and approximate dissections can be done for $\mathrm{Ph_2CHOPNB}$ and $(p\text{-}\mathrm{ClC_6H_4})_2\mathrm{CHOPNB}$. In the case of the first-named, $\delta\Delta G^\ddagger$ values (relative to 80E as standard solvent) were reckoned from the extrapolated 25 °C rate constants, whilst for the other two compounds the 100 °C rate constants were employed. Values of ΔG_t° for reactants relative to 80E were calculated[30] from the measured molar solubilities at 25 °C, a temperature at which the substrates do not react in the time needed for equilibrium. These quantities, together with the derived values of $\Delta G_t^\circ(\mathrm{TS})$, are shown in Table 8.

TABLE 8

Free energies of transfer (molar scale)[a] of initial and transition states from 80E to other ethanol–water solvents at 25 °C[b]

Solvent	80E	70E	60E	50E
(i) $(p\text{-}\mathrm{MeC_6H_4})_2\mathrm{CHOPNB}$				
ΔG_t°	0.00	0.75	1.16	2.11
ΔG_t° (TS)	0.00	0.35 (0.04)	0.25 (0.09)	0.94 (0.53)
(ii) $\mathrm{Ph_2CHOPNB}$				
ΔG_t°	0.00	0.51	1.11	1.83
ΔG_t° (TS)	0.00	(−0.07)	(−0.07)	(0.09)
(iii) $(p\text{-}\mathrm{ClC_6H_4})_2\mathrm{CHOPNB}$				
ΔG_t°	0.00	0.56	1.35	2.23
ΔG_t° (TS)	0.00	(−0.05)	(0.28)	(0.73)

[a] In kcal mol^{-1}. [b] Values in parentheses were calculated from free energies of activation measured at 100 °C.

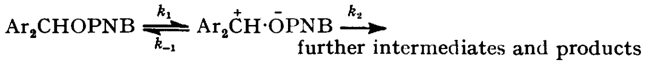
Exact analysis is possible only for $(p\text{-}\mathrm{MeC_6H_4})_2\mathrm{CHOPNB}$ where rate constants and solubilities at the same temperature are available. However, values in parentheses based on rate constants of 100 °C suggest that no serious discrepancies are occasioned by the temperature difference. The pattern that emerges is that rate changes are dominated by initial state effects, as is common, and that overall destabilization of the TS occurs as solvents become more aqueous.

While this is the pattern seen for the $S_\mathrm{N}2$-like substrates in Table 7 (as are the lower than expected m_WG values recorded in Table 5) we are loath to involve solvent assistance as an explanation. Large cavity effects, not particularly well compensated by electrostatic stabilization, are clearly playing an important role and it is not difficult to see why. The extension of the $\mathrm{C_\alpha \cdots O}$ bond as the TS forms necessarily requires a larger cavity, but even with this extension the dipolar partial bond should remain well shielded from solvent molecules[29] by the three phenyl groups surrounding it. On the other hand the negative end of the TS dipoles of the substrates assembled in Table 7 (all halides) should be more accessible to stabilizing solvational forces, and so any analogy between the latter solvolyses and the present system is tenuous at best. It is significant that the lowest m_WG value observed for a *bona fide* unassisted (k_c) solvolysis in ethanol–water mixtures pertains to vinyl cation formation from a highly elaborated tosylate.[36] There is of course a better chance of m_{WG} *versus* Z correspondence when a halide leaving group is employed. Harris and Shafer find that m_{WG} is indeed dependent upon substituents in the diarylmethyl chloride series.[13]

Thus m_{WG} in the present situation is in no way a measure of relative TS polarity; neither is it certain that the constancy of m_{WG} with variation of *para*-substituent presages TS immutability.

Other lines of attack on the question of solvent assistance are equally fruitless. While the Q and l values in Table 6 are compatible with a moderate amount of solvent assistance, it must be emphasized that non-zero values of l and non-unit values of Q will arise automatically whenever m is less than unity. Solvent assistance is of course not the only explanation for $m < 1.0$; shielding of the transition state dipole from the solvent [29] has already been mentioned as a possible cause. As a further example of spurious solvent nucleophilicity parameters we cite the case of cyclo-octyl tosylate: $m_{WG} = 0.73$ in ethanol–water mixtures and hence from equation (2), $l = 0.28, m = 0.80$.[37,38] The modest amount of solvent assistance suggested is, however, negated by another and more sensitive mechanistic probe to be mentioned in the next section; an early and unassisted transition state is apparently the result of steric assistance to ionization.[38]

There is one but one piece of evidence that may have some bearing on the question of solvent assistance. We regard solvent assistance as having the same status as the tool of increasing electron demand; [39] when substituents or intrinsic structural factors cause a destabilization of an incipient carbocationic centre the response of the system will be to seek electron density either internally (participation) or externally (from nucleophilic solvent assistance). Thus $(p\text{-ClC}_6\text{H}_4)_2\text{CHOPNB}$ is the substrate in the present set whose solvolysis is most likely to require solvent assistance. It may therefore be significant that points for this reaction lie slightly above the linear Hammett plot determined by the other substrates, and to a greater extent in the more nucleophilic ethanol-rich solvents. This is consistent with the incursion of a solvent-assisted component.



$$\text{Ar}_2\text{CHOPNB} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Ar}_2\overset{+}{\text{C}}\text{H}\cdot\overset{-}{\text{O}}\text{PNB} \xrightarrow{k_2} \text{further intermediates and products}$$

$$k_{obs} = \frac{k_1 k_2}{k_{-1} + k_2}$$

SCHEME

An alternative reationalization in terms of an internal return mechanism (Scheme) can be offered. In one limit ($k_{-1} \gg k_2$), $k_{obs} = k_1k_2/k_{-1}$ and internal return is important. In the other limit ($k_{-1} \ll k_2$), $k_{obs} = k_1$ and internal return is not competitive. If the solvolysis to return ratio, k_2/k_{-1}, is markedly substituent-dependent it is conceivable that a curved Hammett plot will result. Our reasoning is that if substrates containing electron donors favour return over solvolysis, ρ_{obs} will be the sum of ρ_1, pertaining to the ionization step k_1, and ρ_{RS} pertaining to the partitioning of ion pairs between further ionization and/or solvolysis. If the k_2 step corresponds to further ionization and if the k_{-1} step is close to diffusion control, $\rho_{RS} \approx \rho_2$, with ρ_2 negative. Hence ρ_{obs} will be more negative than ρ_1. As the ion pair becomes less stable (increasing σ^+) ρ_2 should approach closer to zero if the RSP operates and ρ_{obs} should become less negative as it approaches closer to ρ_1. Thus the slight but real curvature in the present Hammett plots can be rationalized on the basis of the operation of the RSP on individual steps of an internal return mechanism. The explanation is plausible in terms of the substituent dependence of *external* return,[40] and the same dependence of k_2/k_{-1} on substituents is required if the Harris and Shafer results on diarylmethyl chloride solvolysis are to be explained on an internal return basis.[13] It will of course be necessary to explain the insensitivity of ρ_{obs} to changes in solvent polarity using the same mechanism, and we return to this question later. We must first distinguish between the two alternatives above.

The Trifluoroethanol-Water Probe.—The previous section has shown that the probes employed are not sensitive to any one particular factor and are not therefore capable of answering the question as to the reality or otherwise of solvent assistance. Raber, Harris, and their associates have developed a sensitive probe for detection of solvent assistance.[42,43] If a substrate solvolyses by rate-limiting ionization, $\log k$ for rates measured in both ethanol–water (E–W) and trifluoroethanol–water (TFE–W) solvent mixtures should correlate linearly with $\log k$ for 1-adamantyl bromide solvolysis (a model k_c substrate) in the same solvents. If on the other hand nucleophilic solvent assistance is important, separate E–W and TFE–W lines should result for the reason that addition of water to ethanol increases solvent polarity but affects solvent nucleophilicity only marginally, whilst addition of water to trifluoroethanol increases both polarity and nucleophilicity.[42,44] Thus the TFE–W line should lie below the E–W line, have a greater slope, and intersect with it at the point corresponding to pure water as solvent. The fact that the latter requirement is not always observed [44] is of little importance in the present context since highly aqueous media have been avoided.

The plot for the solvolysis of Ph_2CHOPNB (TFE–W results from Table 1, E–W results from ref. 18, 1-adamantyl bromide rate constants from refs. 42 and 45) is shown in Figure 1. The somewhat surprising result is that neither of the Raber–Harris patterns is reproduced. The TFE–W points here lie above the E–W line and the slope is smaller than that of the E–W line. The absence of nucleophilic solvent assistance is however indicated by the relative insensitivity of the TFE–W rates to the proportion of the nucleophilic aqueous component of the solvent. We suggest that in the enforced absence of nucleophilic solvent assistance of any magnitude, leaving group departure is aided by electrophilic assistance (hydrogen bonding) in strongly electrophilic solvents such as TFE. Thus the polarity increase occasioned by the progressive introduction of water is accompanied by

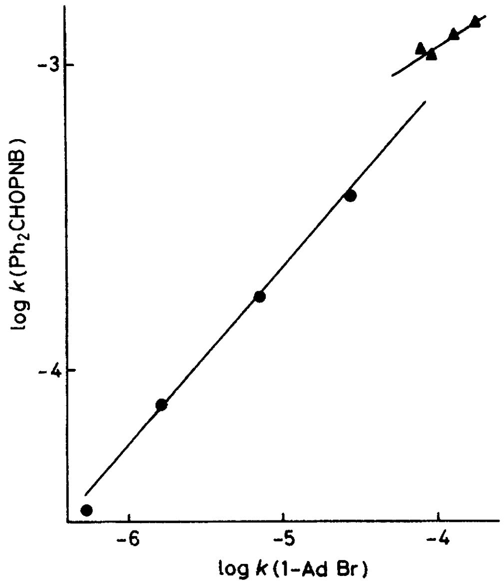


FIGURE 1 The trifluoroethanol–water probe for the solvolysis of $Ph_2CHOPNB$. Closed circles, ethanol–water rates; triangles, trifluoroethanol–water

a decrease in electrophilicity, and rates are relatively insensitive to solvent composition. Similar patterns have been observed in other solvolyses, and identical explanations have been advanced.[44,46] A clearer picture should however result if leaving groups of the probe and model reactions are identical or similar.[47] In Figure 2 we employ 2-adamantyl tosylate as the model k_c substrate (rate constants from refs. 22 and 25), and plot log$k$ ($Ph_2CHOPNB$) against y_{OTs}. A strictly linear plot now results (m_{OTs} 0.82 ± 0.02, r 0.9983), which dispels any suspicion that nucleophilic solvent assistance accompanies the solvolysis of $Ph_2CHOPNB$ in these solvent systems.

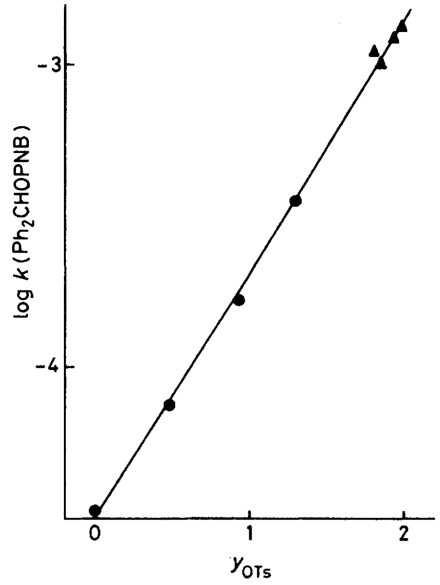


FIGURE 2 Plot of log$k$ for solvolysis of $Ph_2CHOPNB$ in ethanol–water (closed circles) and trifluoroethanol–water (triangles) mixtures against y_{OTs}

If this is accepted it is now difficult to defend the suggestion that diarylmethyl chlorides solvolyse with assistance,[13] since chloride is a better leaving group than p-nitrobenzoate and should require less external push to depart. Indeed, studies of solvolysis of $(p\text{-ClC}_6H_4)_2CHCl$ in TFE–EtOH mixtures[48] show that log$k$ is linearly correlated with log$k$ for 1-adamantyl bromide (a suitable k_c model)[44] over the entire solvent range (slope 0.86). And most importantly the trends in m_{WG} and α-k_H/k_D for the Ar_2CHCl reactions become hard to interpret in RSP terms if solvent assistance is not operative.

An Internal Return Mechanism.—Dismissal of the solvent assistance possibility leaves three simple possibilities open for consideration. One of these, an external return mechanism, is easily dismissed. No common ion rate depression occurs, since accurate first-order kinetics are obtained over several half-lives in all reactions.

The second possibility is that the unassisted process has simple ionization (the k_1 step in the Scheme) as rate-limiting step. If this is the case, and if m and ρ are temporarily accepted as indices of TS character, we must then accept that selectivity is independent of reactivity, in contradiction to the RSP, and that TS character is invariant. We have already suggested that m in the present case is at best an ambiguous indicator, and it has previously been pointed out that ρ has dubious status as a TS index in cases where steric crowding about the reaction centre forces the benzene ring out of optimal orientation with respect to the developing p-orbital.[4] With the present substrates this is indeed a strong possibility; a further complication is the impossible requirement for two rings to achieve coplanarity in order to allow full resonance interaction with the reaction centre. Our assumption of substituent effect additivity, forced upon us because of the absence of a wider range of substituents, is thus open to doubt.

Finally, we consider an internal return mechanism (Scheme).* There exists independent evidence that internal return can possibly occur in the solvolyses of $Ar_2CHOPNB$ compounds in acetone–water solvents, in that oxygen scrambling accompanies solvolysis.[49] There is debate on whether oxygen scrambling reaction and solvolytic reactions utilize identical pathways and therefore intermediates[19b,27,49,50] and we are in no position to contribute since the extent of oxygen scrambling in ethanol–water solvents is unknown. We can be reasonably sure that it will be of lesser importance than in acetone–water,[27,51] and in support of this we note that external return accompanies solvolysis of Ph_2CHCl in acetone–water but is absent when ethanol–water solvents are used.[13]

Evidence in the following paper strongly suggests that

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* It is sometimes implicitly assumed that internal return and solvent assistance are mutually exclusive processes. Bentley and his co-workers[27] have recently reiterated that this is not so; there is no reason why an ion pair formed with solvent assistance cannot suffer internal return.

an ion pair, capable of partitioning between return and further ionization, is involved in $Ar_2CHOPNB$ solvolysis. Thus the process illustrated in the Scheme is to be the basis of explanation of the present results. We again consider the two limiting cases.

In the limit of maximum return, $k_{-1} \gg k_2$, and to a good approximation, $\rho_{obs} = \rho_1 + \rho_2$, with both the latter quantities being negative. In the case of invariant solvent nucleophilicity this limit is expected in solvents of low polarity. The other limit ($k_{-1} \ll k_2$) corresponds to no internal return and is expected to be approached in solvents of higher polarity.[27] If the RSP applies to the k_1 ionization step, ρ_1 should become less negative as solvent polarity increases. It is a reasonable prediction that ρ_2 will become more negative as solvent polarity increases; the ion pair will be more stable and application of the RSP requires that its fate should be more sensitive to substituent variation. If the trends in ρ_1 and ρ_2 balance each other, ρ_{obs} will be constant despite the overall reactivity increase occasioned by the solvent change. It is of course possible that ρ_{obs} may increase or decrease with changing solvent polarity depending on the interplay between ρ_1 and ρ_2. The important point to recognise is that, paradoxically, a constant value of ρ_{obs} may obtain in a situation where reactivities are influenced by solvent change *as a result of RSP effects*. This can only occur in a multistep mechanism, and thus the present work graphically illustrates the caveat that detailed mechanistic information concerning a given solvolysis reaction must be available before that reaction is used to investigate the veracity or otherwise of the RSP.

If we are to uphold the present results as an example of true RSP behaviour being obscured by the multistep nature of the reaction we must demonstrate that ion pair intermediates, formed without solvent assistance, partition between return and further ionization. This is the subject of the following paper.

In conclusion we point out that consideration of the RSP is ultimately intended to be of assistance to the synthetic chemist pondering the choice of reagents, solvents, and conditions. In the practical sense the present results could not be of less interest; their impact concerns the more esoteric question of the corollary to the RSP.

EXPERIMENTAL

Details of substrate preparation and purification, and the kinetic procedure have already appeared.[20] Solubilities of the substrates tabulated in Table 3 were measured by preparing saturated solutions at 25 °C and withdrawing supernatant solutions with a pre-warmed pipette at various time intervals. The ester concentrations were measured spectrophotometrically with reference to calibration lines, and the solubilities were taken from the constant concentration values. Check experiments revealed that no *p*-nitrobenzoic acid was released in the time needed for equilibration.

Trifluoroethanol was purified by a standard method [52] and aqueous mixtures were made up by weight.

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