A Rate and Product Study of the Effect of Solutes upon the Solvolysis of Benzyl Toluene-*p*-sulphonate in Aqueous Trifluoroethanol

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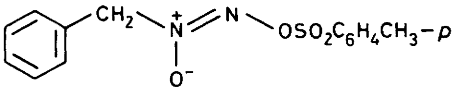
The effects of several electrolytes, including sodium perchlorate, thiocyanate, acetate, and halides, upon the rate and products of solvolysis of benzyl tosylate in 1 : 1 (v/v) aqueous trifluoroethanol at 25 °C have been investigated. In the absence of any electrolyte, the ratio of benzyl alcohol to benzyl trifluoroethyl ether is only marginally greater than the molar ratio of water to trifluoroethanol in the reaction medium. Sodium perchlorate gives rise to a kinetic salt effect but no detectable perturbation of the product ratio. Thiocyanate, iodide, and bromide lead to second-order rate terms and the formation of substitution products. Thiocyanate, the most effective nucleophile used, does not affect the internal ratio of the solvent-derived products. We find no evidence of nucleophilic capture of carbonium ion intermediates formed in prior rate-determining steps. Chloride, acetate, and hydroxide are very weak nucleophiles in this medium and do not lead to overall rate enhancements. Replacing a small proportion of the trifluoroethanol by ethanol leads to the formation of a low yield of benzyl ethyl ether. There is no evidence of benzyl tosylate reacting other than by S_N2 mechanisms, either uncoupled in reactions with solvent and hard nucleophilic solutes, or coupled with soft nucleophiles such as iodide and thiocyanate.

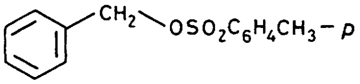
A general technique for investigating reactions which may involve carbonium ions is to employ alternative routes for generating the same putative reactive intermediates, and to attempt to intercept them by nucleophilic solutes. The range of possibilities for generating carbonium ions under broadly comparable solvolytic conditions is not wide, but has been expanded recently by our development of the solvolysis of alkylazoxy tosylates.[1] In order to investigate the effect of aromatic substituents upon this reaction, we began a study of the solvolysis of the known benzylazoxy tosylate (**1**).[2] However, a detailed interpretation of the outcome of this study rests upon a prior understanding of the solvolytic chemistry of benzyl tosylate itself (**2**) under the same conditions.

A methylene group linking a nucleofuge to an aryl residue represents the simplest system for investigating electronic effects upon the displacement of the nucleofuge from the saturated carbon by a nucleophile. Consequently, solvolytic and other substitution reactions of benzyl halides and arenesulphonates have been studied over many years.[3]

In an early investigation, Hammond[4] reported that modest concentrations of nitrate and chloride in aqueous acetone reduced the extent of hydrolysis of benzyl tosylate through the formation of benzyl nitrate and chloride without, at the same time, introducing a second-order term into the rate law. This, and other evidence, was taken to indicate a rate-determining unimolecular ionization followed by trapping of the intermediate benzyl carbonium ion by either solvent or nucleophilic solutes, the classical S_N1 mechanism of Ingold.[5] According to this mechanism, electron-donating substituents such as *p*-methoxy facilitate the initial ionization and hence the overall rate, and electron-withdrawing ones such as *p*-nitro exert an opposite influence. Since electronic effects upon the alternative S_N2 reaction mode are weaker,[3,6] the direct displacement mechanism becomes better able to compete with the S_N1 process as the overall reaction becomes slower. Strongly deactivated benzylic arenesulphonates, or substrates with an unsubstituted benzyl residue bonded to modest or poor leaving groups such as chlorine or trialkylamines, therefore, allowed investigation of the bimolecular substitution in fine detail uncomplicated by a competing mechanism *via* carbonium ion intermediates.[3,7]



(**1**)



(**2**)

Whilst the nature of the solvent and added nucleophiles obviously have some effect, the parent benzyl tosylate itself was regarded as being close to the mechanistic changeover between S_N1 and S_N2 extremes in conventional solvolytic media according to this two-mechanism model.[8,9] Other investigations having regard to a wider range of criteria subsequently indicated that a solvent-induced bimolecular mechanism is predominant for the solvolysis of even quite strongly activated benzylic substrates.[3b,10] Additionally, however, there have been other reports which appear to require mechanisms involving ions and ion-pairs,[11] and the current position is far from clear.[12] Most recently, the lifetime of the unsubstituted 1-phenylethyl carbocation has been estimated to be *ca.* 10^{-11} s in aqueous trifluoroethanol,[13] which is too short for extensive diffusion through the aqueous medium. Since benzyl is a less stable carbonium ion than 1-phenylethyl, and benzyl compounds are sterically more susceptible to bimolecular attack than their 1-phenylethyl analogues, carbonium ion routes in the solvolysis of familiar benzylic substrates have become less credible.

We report here an extension of the early studies on benzyl tosylate itself using 1 : 1 (v/v) water–trifluoroethanol as solvent to facilitate comparison with other recent work. With the knowledge of the results from the 1-phenylethyl system, we took as a working hypothesis that benzyl tosylate reacts under our solvolytic conditions by a solvent-induced S_N2 mechanism, and sought evidence that any appreciable extent of reaction in this highly ionizing medium required a mechanism involving a reactive electrophilic intermediate. We have compared actual analytical results with those calculated from the rate law on the basis of alternative reaction mechanisms and our results require revision of earlier conclusions based upon experiments where this was not done. Additionally, the present investigation was to establish and validate procedures used in the more innovative parallel study of the solvolysis of benzylazoxy tosylate with a view to identifying the reactive benzylic intermediate(s) implicated in that reaction.[2]

Method

Reaction mixtures were analysed directly by h.p.l.c. using naphthalene as an internal standard when absolute yields were required. The relative response of the h.p.l.c. u.v. detector towards different reaction products was determined by analysis of standard solutions of products using procedures and conditions identical with those employed in the analysis of actual solvolysis mixtures. Trifluoroethanol (TFE)–water 1:1 (v/v) is conveniently prepared and corresponds to a molar ratio of 1:4.04. A medium comprising water–trifluoroethanol–ethanol [50:47:3 (v/v); 0.80:0.185:0.015 (mol fraction)] was also used. This corresponds to replacing a small proportion of the weakly nucleophilic TFE by an alcohol which is of comparable nucleophilicity to water but not appreciably different in molecular size and structure from TFE.

Experimental

Benzyl alcohol, ethanol, and trifluoroethanol were Aldrich Gold Label grade or the equivalent and used without further purification; water for solvolysis media was distilled using glass apparatus. Upon mixing 5.00 cm^3 of each of TFE (d 1.376 g cm^{-3}) and water (or aqueous sodium acetate), 9.71 cm^3 of 1:1 (v/v) medium was obtained which is 28.6 and 7.09 mol dm^{-3} in water and trifluoroethanol, respectively. Corresponding solvent molar concentrations in the 50:47:3 (v/v) water–trifluoroethanol–ethanol are 28.6, 6.66, and 0.531 mol dm^{-3} respectively. Upon mixing 5.00 cm^3 of each of acetone and aqueous sodium acetate, 9.62 cm^3 of 1:1 (v/v) medium was obtained which is 28.9 mol dm^{-3} in water. All solvolysis media were checked by u.v. and h.p.l.c. Authentic samples of benzyl ethyl ether and benzyl trifluoroethyl ether (for h.p.l.c. identification and development of the analytical method) were prepared by solvolysis of benzyl tosylate (or bromide) in pure ethanol or trifluoroethanol.

Benzyl Toluene-p-*sulphonate*.—This compound was prepared by the Tipson[14] procedure, m.p. 57—58 °C (from diethyl ether) (lit.,[15] 58.5—58.9 °C); $\delta(CDCl_3)$ 7.72, 7.20 (4 H, ABq, $J = 8$ Hz), 7.20 (5 H, s), 4.99 (2 H, s), and 2.38 (3 H, s).

Determination of the H.p.l.c. Detector's Molar Response Factor (*M.r.f.*) *for Benzyl Alcohol* versus *Naphthalene*.—Standard solutions of benzyl alcohol and naphthalene in slightly aqueous methanol were analysed by h.p.l.c. using the conditions employed in the analysis of solvolysis reactions.

$$\text{m.r.f.} = \frac{\text{PhCH}_2\text{OH integration}}{\text{naphthalene integration}} \times \frac{\text{molarity of naphthalene}}{\text{molarity of benzyl alcohol}}$$

$$= 0.0572\ (\pm 0.0005)$$

Subsequent analysis of the benzyl alcohol produced from an accurately weighed amount of benzyl tosylate in a standard solution of naphthalene in aqueous acetone corroborated the above result.

Indirect determination of the m.r.f. for benzyl trifluoroethyl ether, benzyl thiocyanate, and benzyl acetate versus *naphthalene*. Accurately weighed amounts of benzyl tosylate were solvolysed in standard solutions of (i) naphthalene in aqueous trifluoroethanol, (ii) naphthalene and sodium thiocyanate in aqueous acetone, and (iii) naphthalene and sodium acetate in aqueous acetone. The reaction mixtures were analysed by h.p.l.c., and m.r.f. values of 0.0641 (benzyl trifluoroethyl ether *versus* naphthalene, 1.12 *versus* benzyl alcohol), 0.308 (benzyl thiocyanate *versus* naphthalene, 5.38 *versus* benzyl alcohol), and 0.0662 (benzyl acetate *versus* naphthalene, 1.16 *versus* benzyl alcohol) were obtained.

Solvolysis of Benzyl Tosylate.—(i) *Kinetics*. Rates of solvolysis of benzyl tosylate (1—2 mg) in the appropriate medium (*ca*. 2.5 cm^3) were measured by monitoring the decrease in u.v. absorbance in the thermostatted cell compartment of a Gilford spectrophotometer linked to a chart recorder in the normal way. Reactions in the presence of electrolytes were carried out under pseudo-first-order conditions. First-order rate constants were calculated by the Kezdy–Swinbourne method with a Commodore VIC-20 microcomputer using 20—50 data points covering *ca*. 5 half-lives.[16] Early results were rounded off to $0.1 \times 10^{-3}\ s^{-1}$, later ones to $0.05 \times 10^{-3}\ s^{-1}$.

(ii) *Product analysis*. A solution (4.00 cm^3) made up from sodium perchlorate (1.00 mol dm^{-3}, 5.00 cm^3) and trifluoroethanol (5.00 cm^3) was added to recrystallized benzyl tosylate (5—30 mg). After the reaction mixture had been vigorously shaken, samples were transferred to screw-capped h.p.l.c. vials for analysis. In place of the standard sodium perchlorate, aqueous solutions of other salts made up to a total ionic strength of 1 mol dm^{-3} were also used (those containing sodium iodide were deoxygenated by argon bubbling). If absolute rather than relative yields of products were required, a standard solution of naphthalene in trifluoroethanol (typically *ca*. 2×10^{-3} mol dm^{-3}) and an accurately weighed amount of benzyl tosylate (15—30 mg) were used. For solvolyses containing ethanol, a solution made up from trifluoroethanol (47.0 cm^3) and absolute ethanol (3.0 cm^3) was used in place of pure trifluoroethanol. All reaction mixtures were analysed directly using aqueous methanol gradient elution with a reverse-phase C-18 h.p.l.c. column in a Waters system including a WISP autoinjector and u.v. detector set at 257 nm. Integrated chromatograms were recorded on a Waters Data Module. Reactions were carried out at least twice and each product mixture was normally analysed 5—10 times. When absolute yields were measured, the total recovery was usually in the range 95—105%. Mean values for one product mixture were normalized to 100% before being averaged with results from a duplicate reaction. Several reaction mixtures were re-analysed over several days, which established that $PhCH_2OH$, $PhCH_2OCH_2CF_3$, and $PhCH_2SCN$ were quite stable to the reaction conditions. There was evidence, however, that the naphthalene concentration decreased slowly over such a period. This phenomenon was not investigated, but only freshly prepared standard solutions of naphthalene were used for quantification of product yields.

Results

Rate results are given in Tables 1 and 2 and some are illustrated in Figures 1 and 2; product ratios are shown in Tables 3 and 4. Sodium perchlorate increases the solvolytic rate constant without, at the same time, significantly affecting the product distribution. Perchloric acid has about the same rate effect. Sodium acetate alone causes virtually no rate effect so, when its concentration is increased at constant ionic strength maintained by sodium perchlorate, the observed rate constants decrease. The same was found for sodium hydroxide. Moreover, 0.5 mol

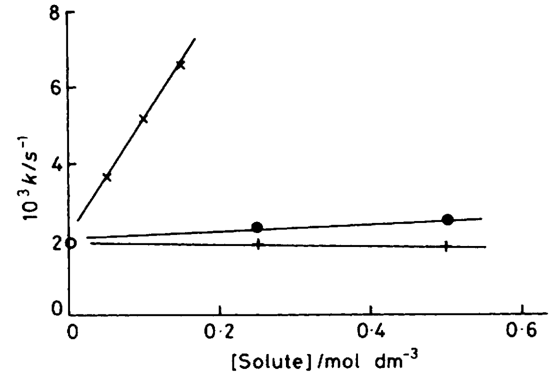


Figure 1. Effect of solutes upon the rate constants for solvolysis of $PhCH_2OTs$ in 1:1 (v/v) H_2O–TFE at 25 °C: ●, $NaClO_4$; ×, NaI; +, NaOAc

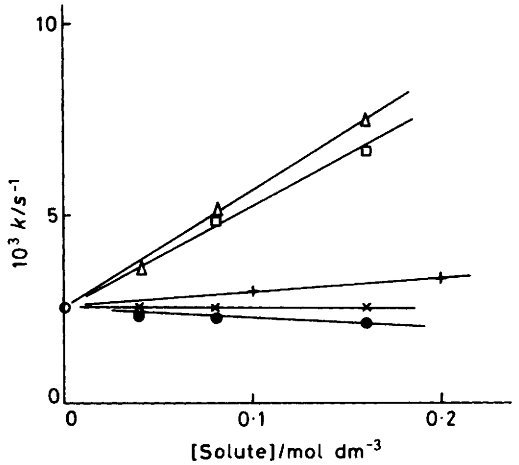


Figure 2. Rate constants for the solvolysis of $PhCH_2OTs$ in 1:1 (v/v) H_2O–TFE at ionic strength 0.5 mol dm^{-3} and 25 °C: ●, NaOH; ×, NaCl; +, NaBr; △, NaSCN; □, NaI

Table 1. Effect of solutes upon the rate constants for the reaction of benzyl tosylate in 1:1 (v/v) water–trifluoroethanol at 25 °C[a]

Solute	Concentration (mol dm^{-3})	$10^3k_{obs}/s^{-1}$
None		1.9
$NaClO_4$	0.25	2.3
$NaClO_4$	0.50	2.50[b]
NaI[c]	0.05	3.6_5[d]
NaI[c]	0.10	5.2
NaI[c]	0.15	6.6[d]
NaOAc	0.25	1.9
NaOAc	0.50	1.8

[a] Results rounded off to 0.1 × 10^{-3} s^{-1}. [b] Mean of three independent determinations rounded off to 0.05 × 10^{-3} s^{-1}. [c] k_I 31 × 10^{-3} dm^3 mol^{-1} s^{-1} ($r > 0.998$). [d] Mean of two independent determinations.

dm^{-3} NaOAc led to only minimal formation of benzyl acetate although the slight increase in the proportion of trifluoroethanol-derived solvolysis product is almost certainly real. [In contrast, an appreciable yield of $PhCH_2OAc$ was formed from 0.5 mol dm^{-3} NaOAc in 1:1 (v/v) water–acetone, Table 3 footnote *e*.]

The powerfully nucleophilic sodium thiocyanate and iodide have substantial kinetic effects and lead to the formation of high yields of benzyl thiocyanate and iodide. The experimental yield of $PhCH_2SCN$ from $PhCH_2OTs$ at 0.08 mol dm^{-3} NaSCN and total ionic strength 0.5 mol dm^{-3} is, if anything, lower (45%) than the calculated value (51%) based upon the solvolytic and second-order rate constants given in Table 2. For iodide at 0.048 mol dm^{-3}, the measured yield of $PhCH_2I$ (37%) is also somewhat lower than that calculated from the rate constants (44%). [Sodium thiocyanate was also found to be powerfully nucleophilic towards $PhCH_2OTs$ in aqueous acetone, Table 3 footnote *e*.]

Table 2. Rate constants for the solvolysis of benzyl tosylate in 1:1 (v/v) water–trifluoroethanol at constant ionic strength (0.5 mol dm^{-3}) and 25 °C[a]

Solute	Concentration (mol dm^{-3})	$10^3k_{exp}/s^{-1}$
None		2.50[b]
NaOH	0.04	2.45
NaOH	0.08	2.25
NaOH	0.16	2.15
$HClO_4$	0.10	2.40
$HClO_4$	0.20	2.75
NaCl[c]	0.04	2.50
NaCl[c]	0.08	2.50
NaCl[c]	0.16	2.55
NaBr[d]	0.1	3.00
NaBr[d]	0.2	3.30
NaOAc	0.15	2.20
NaOAc	0.25	2.25
NaOAc	0.40	2.05
NaOAc	0.50	1.80
NaSCN[e]	0.04	3.55
NaSCN[e]	0.08	5.10
NaSCN[e]	0.16	7.50
NaI[f]	0.08	4.80
NaI[f]	0.16	6.70

[a] Ionic strength made up to 0.5 mol dm^{-3} with sodium perchlorate; results rounded off to 0.05 × 10^{-3} s^{-1}. [b] Mean of three independent determinations. [c] $PhCH_2Cl$ detected as reaction product. [d] k_{Br} 4 × 10^{-3} dm^3 mol^{-1} s^{-1}. [e] k_{SCN} 32 × 10^{-3} dm^3 mol^{-1} s^{-1} ($r > 0.998$). [f] k_I 26 × 10^{-3} dm^3 mol^{-1} s^{-1}; k_{obs} 16 × 10^{-3} s^{-1} at [I^-] 0.5 mol dm^{-3} is calculated from these results which compares well with the value of 18 × 10^{-3} dm^3 mol^{-1} s^{-1} at [I^-] 0.5 mol dm^{-3} calculated from the results in Table 1 (not obtained at constant ionic strength).

Sodium bromide leads to the formation of benzyl bromide and a modest second-order rate term at constant ionic strength; sodium chloride also leads to substitution product, $PhCH_2Cl$, but causes no rate effect (as was reported earlier for reactions in aqueous acetone[4]).

The ratio of benzyl alcohol to benzyl trifluoroethyl ether in 1:1 (v/v) H_2O–TFE is unaffected by the presence or nature of non-basic solutes, being constant (within experimental error) at just over 4:1, the molar ratio of the two solvent components. The effect of the weakly basic sodium acetate in increasing the proportion of $PhCH_2OCH_2CF_3$ at the expense of $PhCH_2OH$ was noted above. When a small proportion of the trifluoroethanol was replaced by ethanol, a small yield of benzyl ethyl ether was obtained (Table 4). The introduction of 0.08 mol dm^{-3} NaSCN into this ternary solvent system was sufficient to reduce the solvolytic reaction by about half yet, within the solvolysis yield, the relative proportions of the three products remain unchanged.

In Table 5 we have compared the nucleophilicities of SCN^-, I^-, Br^-, Cl^-, AcO^-, and trifluoroethanol with water towards $PhCH_2OTs$ in 1:1 (v/v) water–trifluoroethanol, and ethanol with water in the 50:47:3 mixture, all expressed as ratios of second-order rate constants (real or notional). We have used the real second-order rate constants for SCN^-, I^-, and Br^- given in footnotes to Table 2. The overall solvolytic rate constant in 1:1 H_2O–TFE of 2.5 × 10^{-3} s^{-1} at ionic strength 0.5 mol dm^{-3}

Table 3. Products from reaction of benzyl tosylate in 1:1 (v/v) water–trifluoroethanol at 25 °C[a]

Solute	Concentration (mol dm^{-3})	Total ionic strength[b] (mol dm^{-3})	PhCH$_2$OH:	PhCH$_2$OCH$_2$CF$_3$:	PhCH$_2$X
None		0	83	17	0
NaClO$_4$	0.5	0.5	81	19	0
NaSCN[c,e]	0.016	0.5	71	15	14 (17)
NaSCN	0.08	0.5	46	9	45 (51)
NaCl[d]	0.5	0.5	59	14	27
NaI[c]	0.012	0.012	70	15	15 (16)
NaI	0.048	0.048	53	10	37 (44)
NaOAc[e]	0.05	0.05	80	19	$\leqslant$1
NaOAc	0.5	0.5	76	22	$\leqslant$2

[a] Estimated errors ±2%. [b] Total ionic strength = [NaClO$_4$] + [NaX]. [c] The yields of PhCH$_2$X in parentheses are the values calculated from the rate law k_{obs}/s^{-1} = 2.5 × 10^{-3} + k_x [NaX]. [d] The ratio PhCH$_2$OH:PhCH$_2$OCH$_2$CF$_3$ = 81:19 is reliable, but the normalized yields are based upon a molar response factor of 1.22 for PhCH$_2$Cl:PhCH$_2$OH at 257 nm calculated from interpolated molar absorptivities in aqueous ethanol (T. W. Campbell, S. Linden, S. Godshalk, and W. G. Young, *J. Am. Chem. Soc.*, 1947, **69**, 880). [e] In 1:1 (v/v) aqueous acetone, the following relationships between electrolyte concentration and product analysis were obtained: 0.5 mol dm^{-3} NaSCN, 4% PhCH$_2$OH + 96% PhCH$_2$SCN; 0.15 mol dm^{-3} NaSCN, 8% PhCH$_2$OH + 92% PhCH$_2$SCN; 0.5 mol dm^{-3} NaOAc, 62% PhCH$_2$OH + 38% PhCH$_2$OAc.

Table 4. Products from reaction of benzyl tosylate in 50:47:3 (v/v) water–trifluoroethanol–ethanol. Ionic strength 0.5 mol dm^{-3}, 25 °C[a]

[NaSCN]/ mol dm^{-3}	PhCH$_2$OH:	PhCH$_2$OC$_2$H$_5$:	PhCH$_2$OCH$_2$CF$_3$:	PhCH$_2$SCN
0	78	4	18	0
0.08[b]	40	2	8	51

[a] Total ionic strength = [NaSCN] + [NaClO$_4$]. [b] Within the solvent-derived product, PhCH$_2$OH:PhCH$_2$OC$_2$H$_5$:PhCH$_2$OCH$_2$CF$_3$ = 80:4:16.

Table 5. Second-order rate constant ratios for benzyl tosylate in 1:1 (v/v) water–trifluoroethanol at ionic strength 0.5 mol dm^{-3} and 25 °C

k_{SCN}/k_{H_2O}	k_I/k_{H_2O}	k_{Br}/k_{H_2O}	k_{Cl}/k_{H_2O}	k_{OAc}/k_{H_2O}	k_{EtOH}/k_{H_2O}	k_{TFE}/k_{H_2O}
452[a] (1 800[b])	367[a]	56[a]	26[c]	1.5[c] (35[b])	2.8[d,e]	0.95[f,e]

[a] Calculated from rate and product analytical results and based upon a second-order rate constant between PhCH$_2$OTs and water in 1:1 H$_2$O–TFE of k_{H_2O} 7.08 × 10^{-5} dm^3 mol^{-1} s^{-1}. [b] Approximate results calculated from product analyses given in footnote *e* of Table 3 and relative molarities of the nucleophile and water in 1:1 (v/v) aqueous acetone. [c] Approximate result calculated from the product analyses in Table 3 and the relative molarities of nucleophile:water = 0.5:28.6 in 1:1 (v/v) H$_2$O–TFE (0.5 mol dm^{-3}) in NaCl or NaOAc. [d] Calculated for 50:47:3 (v/v) H$_2$O–TFE–EtOH from product analyses in Table 3 and the relative solvent molarities 28.6:6.66:0.531. [e] The ratio of these gives k_{EtOH}/k_{TFE} 2.9 in agreement with the value 2.8 calculated directly from product analysis for PhCH$_2$OCH$_2$CH$_3$:PhCH$_2$OCH$_2$CF$_3$ in the 50:47:3 medium. [f] Calculated from the product analyses in Table 3 and relative molarities of H$_2$O and TFE in the 1:1 medium.

(NaClO$_4$) can be dissected into first-order components for separate reactions with water and with trifluoroethanol from the product analysis (Table 3). The value for water, 2.0 × 10^{-3} s^{-1}, can then be converted into a notional second-order rate constant using the molar concentration of water in the 1:1 (v/v) medium (28.6 mol dm^{-3}), 7.1 × 10^{-5} dm^3 mol^{-1} s^{-1} at ionic strength 0.5 mol dm^{-3} (NaClO$_4$).* This second-order rate constant then allows reactivity ratios for SCN$^-$, I$^-$, and Br$^-$ *versus* water to be calculated.

The ratios in Table 5 for Cl$^-$, AcO$^-$, trifluoroethanol, and ethanol were obtained more simply from the product ratios and the molar concentrations of each nucleophile relative to water, the first three in the 1:1 (v/v) medium (molar ratio, H$_2$O–TFE 4.04:1), and the ethanol in the 50:47:3 (v/v) mixture (molar ratio, H$_2$O–EtOH 54:1). By this latter technique, approximate reactivities of SCN$^-$ and AcO$^-$ relative to water towards PhCH$_2$OTs in 1:1 (v/v) water–acetone were also calculated and are shown in parentheses in Table 5.

The former method of calculating the relative reactivities of nucleophiles towards PhCH$_2$OTs using second-order rate constants has the merit of not relying upon a single experimental product analysis, and the comparison is, in each case, with the same parameter (k_{H_2O} at ionic strength 0.5 mol dm^{-3}, NaClO$_4$). Consequently, comparisons between results for SCN$^-$ and I$^-$ or Br$^-$ using the results of Table 5 are legitimate. However, these reactivity ratios can never quite relate exactly to any given set of real experimental conditions, nor can they be expected to allow an exact calculation of product ratios because of the different effects of sodium perchlorate and the other salts upon the solvolytic rate alone.

The latter method is at least based upon a direct analysis from a solvolysis of PhCH$_2$OTs in the presence of a nucleophilic solute or co-solvent, but, for Cl$^-$ and AcO$^-$, the results are derived from data from single sets of experimental conditions. It would be imprudent to regard the results for Cl$^-$ and AcO$^-$ as anything more than approximate, or to attach too great a significance to comparisons of results for these two nucleophiles with those obtained by the other method.

Discussion

(a) *Effect of Solutes*.—The comparable increases in rates due to sodium perchlorate and perchloric acid seem to be a medium effect upon the solvolytic reaction. However, since sodium acetate and, presumably, sodium hydroxide alone cause no solvolytic rate increase, the 'salt effects' cannot be simply and entirely due in all cases to the altered ionic strength and taken as (empirical) evidence for an ionic mechanism. Whilst a detailed molecular understanding of such specific salt effects is not yet available, both negative and positive effects in comparable reactions have been reported before.[18]

A substantial and more easily interpreted effect is observed for sodium thiocyanate and iodide. These soft Lewis bases lead

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* The assumptions and hopes in ascribing a molar concentration to a solvent in order, for example, to attribute a second-order rate constant to a solvolytic process or to compare the reactivity of a solvent with that of a solute, are identical with those implicit in allocating a conventional pK_{AH} value to an acidic compound such as water when it acts as both proton donor and as solvent.[17]

to appreciable second-order rate terms and to the formation of benzyl thiocyanate and iodide, respectively. The actual yields of these substitution products are no higher than ones calculated from the second-order rate constants, so there is no evidence of a product-forming route *via* a reactive intermediate in addition to the second-order reactions. The results are adequately explained, therefore, by thiocyanate and iodide reacting directly and exclusively with benzyl tosylate in a bimolecular substitution, the familiar S_N2 reaction. As expected, sodium bromide, a weaker nucleophile than iodide or thiocyanate, leads to a smaller second-order rate term and the unmistakable formation of appreciable amounts of the lachrymatory benzyl bromide by the same mechanism. The effect of sodium chloride is interesting. At constant ionic strength maintained by sodium perchlorate, there is no apparent effect upon the overall rate constant, but benzyl chloride is unambiguously formed. An analogous result was previously taken as evidence of an S_N1 mechanism in aqueous acetone[4] but an explanation compatible with a wider body of evidence is now available. Following the trend of sodium iodide and bromide, sodium chloride should lead to the formation of some benzyl chloride through a bimolecular substitution reaction and, consequently, a second-order term in the solvolytic rate law. However, like acetate and hydroxide, the hard chloride anion should have a smaller specific salt effect than perchlorate. So, as chloride replaces perchlorate in the medium at constant ionic strength, the small second-order rate term due to the increasing S_N2 reaction with solute is counterbalanced by the accompanying decreasing composite salt effect upon the solvolytic reaction, and the overall rate constant remains virtually unchanged.

Results in Table 5 for solutes in 1:1 (v/v) H_2O–TFE and 1:1 (v/v) H_2O–Me_2CO also indicate that different solvation of an anion in different solutions, both containing a high proportion of water, affects the partitioning of the electrophile between the anion and water. Thiocyanate is <500 times more effective than water in aqueous trifluoroethanol, whereas it may be up to 2 000 times more effective in aqueous acetone, a four-fold change in selectivity. In contrast, the poor ability of acetate to compete with water for benzyl tosylate in aqueous trifluoroethanol is increased at least 20-fold upon transfer to aqueous acetone. Transfer of thiocyanate from aqueous acetone to aqueous trifluoroethanol clearly causes a smaller depression of its relative nucleophilic activity by enhanced hydrogen-bonding than the corresponding transfer of the harder and more basic acetate.

(b) *The Solvent-induced Reaction.*—The ratio of benzyl alcohol to benzyl trifluoroethyl ether is only marginally greater than the molar ratio of water to trifluoroethanol (4:1) in the 1:1 (v/v) medium and, within experimental error, is independent of the concentration and nature of any added non-basic electrolyte (Table 3). Taking the molar proportions of the solvent components into account, a reactivity ratio of k_{H_2O}/k_{TFE} *ca.* 1.1 is calculated. This is similar to the values obtained for a range of 1-arylethyl chlorides and bromides.[18] Clearly, therefore, with these compounds, water appears to be not significantly more nucleophilic than trifluoroethanol. Indeed, in the presence of sodium acetate, the H_2O–TFE-derived solvolysis product ratio from benzyl tosylate drops to *ca.* 3.5, below the molar ratio of H_2O–TFE in the medium (k_{H_2O}/k_{TFE} *ca.* 0.8_5). This is probably an indication that acetate acts as a general base and catalyses the reaction of trifluoroethanol more effectively than that of water with benzyl tosylate even though it does not itself react directly with benzyl tosylate to any appreciable extent. But the effect is minor and not large enough to be detected in the kinetics of the overall reaction. It is normal for the onset of some facilitating effect such as inter- or intra-molecular catalysis to modify the product distribution before any overall rate enhancement is evident.[19]

When a small proportion of trifluoroethanol is replaced by ethanol (not so much that the bulk solvent properties of the medium are drastically changed), benzyl ethyl ether is produced. The relative yields of the three solvent-derived products are not affected by competition with sodium thiocyanate and, taking the molar proportions of the solvent components into account, we calculate k_{EtOH}/k_{TFE} *ca.* 2.9 and k_{EtOH}/k_{H_2O} *ca.* 2.8. The former, particularly, is a small ratio for compounds of similar type but of substantially different base strengths, and the same as the smallest corresponding value of k_{MeOH}/k_{TFE} reported for a range of 1-arylethyl chlorides and bromides.[18]

Conclusions.—All the present results can be accommodated by benzyl tosylate reacting entirely *via* the S_N2 mechanism. We have evidence against the involvement of reactive intermediates and, therefore, rule out any significant extent of reaction through the benzyl cation (ion-paired or otherwise) in S_N1 reactions. It has already been emphasized, however, that an S_N2 mechanism does not imply a single or invariable transition-state structure.[20,21] Indeed, the appreciably negative ρ values reported earlier for solvolysis of substituted benzyl tosylates indicate activated complexes with very considerable ionic character.[8,21] The very small discrimination in favour of ethanol over water and of water over trifluoroethanol when these are components of the solvent indicate that the reaction is at the uncoupled end of the S_N2 mechanistic range. In accordance with this, hard nucleophilic anions such as acetate and hydroxide introduce no detectable second-order rate term and only as the softness increases along the series chloride, bromide, iodide, and thiocyanate do we observe coupled S_N2 reactions characterized by increasing second-order rate constants. Even so, the relative reactivity between the most and least effective nucleophiles (SCN^- and TFE) taking molar concentrations into account is still only a factor of *ca.* 450 in 1:1 (v/v) trifluoroethanol–water.

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