A study of the mechanism of solvolysis of but-3-enyl bromide (4-bromobut-1-ene) using the extended (two-term) Grunwald–Winstein equation †

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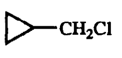
The solvolysis of but-3-enyl bromide at 70 °C follows the S_N2 mechanism over a wide variety of solvents as indicated by a sensitivity to changes in solvent nucleophilicity (l value) of 0.99 ± 0.04, specific rates of solvolysis of about one-half of those for the saturated butyl bromide and a k_{OTs}/k_{Br} ratio in ethanol of 12, essentially identical with the value previously observed for ethanolyses of methyl and ethyl derivatives. There are indications of a minor (about 35%) S_N1 component to the solvolysis in 97% TFE, which becomes dominant in 90% HFIP. Kinetic analysis suggests, consistent with previous product studies, only an approximately 4% S_N2 component to a dominant S_N1 formolysis of the corresponding tosylate.

The observation of homoallylic participation in the solvolyses of cholesteryl derivatives[1,2] led to investigations of the solvolyses of the simplest molecules within which participation of this type could occur: but-3-enyl derivatives, considered in conjunction with the isomeric cyclopropylmethyl and cyclobutyl derivatives. In a study of the solvolyses of the chlorides in 50% ethanol at 50 °C,[3] it was found that cyclopropylmethyl chloride (**1**) was 27 times more reactive than cyclobutyl chloride (**2**) and the but-3-enyl chloride (**3**) reacted extremely slowly. Even at 90 °C, the butenyl chloride underwent solvolysis at only one-third of the rate for cyclobutyl chloride at 50 °C, with a half-life of 5 days. The solvolyses of cyclopropylmethyl and cyclobutyl chlorides[3,4] were shown to involve large degrees of rearrangement, including internal return to rearranged chloride



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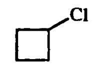

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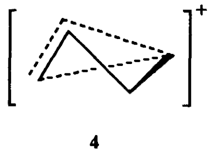
$CH_2{=}CH{-}CH_2{-}CH_2{-}Cl$

3

The carbocation formed in the ionization of a cyclopropylmethyl, cyclobutyl or but-3-enyl derivative was, in early analyses, considered to be the bicyclobutylium ion (**4**),[4–6] which, depending on the site of attack by the nucleophile, could lead to all three types of product. Subsequently, a kinetic study of the influence of multiple substitutions indicated that symmetry existed in the transition state for ionization of cyclopropylmethyl derivatives and an ionization process leading to a bisected cyclopropylmethyl cation was proposed.[7] Although there is also evidence to the contrary,[8] there is a large body of evidence indicating that cyclobutyl derivatives also proceed directly to the cyclopropylmethyl cation in the ionization process.[9,10] Studies of the $C_4H_7^+$ cation by NMR isotopic perturbation and by *ab initio* calculation using extended basis sets and with inclusion of electron correlation have recently been reviewed.[11] Both techniques indicate that the energies of three degenerate bicyclobutylium cations and three rapidly equilibrating cyclopropylmethyl cations are very similar, with the bicyclobutylium ion indicated to be marginally more stable by NMR studies and with the two cations indicated to be energy minima with essentially identical energies by calculation.



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The question arises as to the extent to which homoallylic participation, well documented for cholesteryl derivatives,[1,2,12] operates in the solvolyses of other allylmethyl substrates. A summary[13] of the rates of acetolysis of nine allylmethyl arenesulfonates relative to the corresponding rates for the saturated esters (homoallylic double bond absent) demonstrated in seven instances a modest to large acceleration in the presence of the double bond; in two instances, involving the parent structure and Δ^3-cyclohexenyl tosylate, a small retardation was observed.[14] The retardation by a factor of 2 for the parent systems was exactly the ratio predicted,[6] on the basis of the relative acidities of the corresponding acids, if the double bond does not render anchimeric assistance. Similar retardations were estimated by Streitwieser[15a] for the chlorides in 50% ethanol and for the benzenesulfonates in ethanol and the retardation for ethanolysis of the naphthalene-2-sulfonate[15b] is by a factor of 1.8.

Probably, in part because of a slow solvolysis even at elevated temperatures, the unsubstituted (parent) but-3-enyl derivatives have been less extensively studied than the isomeric cyclopropylmethyl or cyclobutyl derivatives. In an attempt to promote ionization reaction, Servis and Roberts[6] studied, using changes in the integration of the ^1H NMR signals, the solvolysis of but-3-enyl toluene-*p*-sulfonate (tosylate) in 98% formic acid, a solvent of relatively high ionizing power[16] coupled with a relatively low nucleophilicity.[16,17] The rate of formolysis at 50 °C was higher than for the saturated butyl tosylate, but only by a rather modest factor of 3.7. Although it was, unfortunately, necessary to carry out product studies in the presence of sodium formate, extrapolation to zero sodium formate concentration showed that the products from capture by a solvent molecule were extensively rearranged, with 45 ± 5% cyclopropylmethyl formate, 45 ± 5% cyclobutyl formate and only 10 ± 5% but-3-enyl formate. The product

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Table 1 Specific rates of solvolysis of but-3-enyl bromide (**5**), k_5, and butyl bromide (**6**), k_6, at 70.0 °C and solvent nucleophilicity (N_T) and solvent ionizing (Y_{Br}) values from the literature

Solvent[a]	k_5[b]/10^{-7} s^{-1}	k_6[b]/10^{-7} s^{-1}	k_6/k_5	N_T[c]	Y_{Br}[d]
100% EtOH	4.84 ± 0.36[e]			+0.37	−2.4
90% EtOH	8.51 ± 0.34			+0.16	−0.84
80% EtOH[f]	14.5 ± 0.2	31.3 ± 1.7	2.16	0.00	0.00
60% EtOH	33.1 ± 1.6	66.5 ± 3.5	2.01	−0.39	1.26
50% EtOH[g]	43.6 ± 2.7			−0.58	1.88
100% MeOH	7.87 ± 0.24[e]			+0.17	−1.12
90% MeOH	14.4 ± 0.6			−0.01	−0.14
80% MeOH	26.2 ± 0.5	48.8 ± 2.1	1.86	−0.06	0.70
60% MeOH	61.9 ± 3.3			−0.54	2.04
80% Acetone	3.61 ± 0.18			−0.37	−0.7
60% Acetone	20.6 ± 0.6	35.7 ± 2.5	1.73	−0.52	1.03
97% TFE[h]	0.190 ± 0.014			−3.30	2.53
90% TFE[h]	0.53 ± 0.02	1.03 ± 0.05	1.94	−2.55	(2.60)
80% TFE[h]	2.06 ± 0.12			−2.19[i]	2.67
70% TFE[h]	3.32 ± 0.28			−1.98	2.79
60% TFE[h]	5.27 ± 0.27			−1.85[i]	2.91
50% TFE[h]	10.3 ± 0.6			−1.73	3.04
80T-20E[j]	2.44 ± 0.18[e]			−1.76	1.64
40T-60E[j]	3.47 ± 0.31[e]			−0.34	−0.57
90% HFIP[h]	0.60 ± 0.06[k]			−3.84	

[a] Unless otherwise stated, prepared on a volume–volume basis at 25.0 °C, with the other component water, substrate concentration of 0.003–0.004 mol dm^{-3}. [b] All runs performed in duplicate and all of the integrated values are used to obtain an average value and the associated standard deviation. [c] Solvent nucleophilicity values from ref. 17. [d] Solvent ionizing power values from ref. 16. [e] In the presence of 0.0050 mol dm^{-3} 2,6-lutidine. [f] Also value of 2.7 (± 0.4) × 10^{-7} s^{-1} at 50.0 °C. [g] Also value of 6.81 (± 0.43) × 10^{-7} s^{-1} at 50.0 °C. [h] Solvent prepared on weight–weight basis. [i] From D. N. Kevill, H. R. Adolf, A. Wang, D. C. Hawkinson and M. J. D'Souza, *J. Chem. Soc., Perkin Trans. 2*, 1990, 2023. [j] T-E are TFE–ethanol mixtures. [k] Substrate concentration of 0.007 mol dm^{-3}.

ratios were described[6] as being virtually identical with those observed after the formolysis under identical conditions of cyclobutyl tosylate, and both formolyses were considered to proceed *via* bicyclobutylium ion intermediates. Kosower[18] noted, however, that a detailed comparison with the products from formolysis of cyclobutyl tosylate[6] indicates an additional 5% of but-3-enyl formate from the formolysis of but-3-enyl tosylate and he proposed that this discrepancy must be due to a small direct displacement component.

These early studies suggest that in solvents of low or modest ionizing power, such as ethanol, 50% ethanol, or acetic acid, the mechanism of solvolysis of but-3-enyl arenesulfonate or chloride is S_N2. However, studies in formic acid (considerably higher ionizing power and fairly low nucleophilicity) suggest that the major pathway in the solvolysis of but-3-enyl tosylate is S_N1, but with an indication of a small residual S_N2 component. These observations suggest that this is a solvolysis which can be usefully considered in terms of the extended Grunwald–Winstein eqn. (1),[19,20] especially if fluoro-alcohol-containing

$$\log(k/k_o) = lN + mY + c \qquad (1)$$

solvents, only just being introduced[21] and rarely used in kinetic studies at the time of the earlier publications, are included. In eqn. 1, k and k_o are the specific rates of solvolysis of the substrate in a given solvent and in the standard solvent (80% ethanol), respectively, m is the sensitivity to changes in solvent ionizing power (Y), l is the sensitivity to changes in solvent nucleophilicity (N) and c is the value for the residual.

A kinetic study of the solvolysis of but-3-enyl bromide (**5**) in a variety of hydroxylic solvents is reported and the data are analysed in terms of the extended Grunwald–Winstein equation. For several of these solvents, the specific rate of solvolysis of butyl bromide (**6**) is determined and compared with that for **5**. Conclusions are drawn concerning the mechanism of solvolysis of **5**.

$CH_2{=}CH{-}CH_2{-}CH_2Br$ $CH_3CH_2CH_2CH_2Br$

5 **6**

Results

Solvolyses of but-3-enyl bromide (5)

Specific rates of solvolysis have been determined at 70.0 °C in the following aqueous–organic solvents: 100–50% ethanol (five compositions), 100–60% methanol (four compositions), 80–60% acetone (two compositions), 97–50% 2,2,2-trifluoroethanol (TFE; six compositions) and 90% 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). A study was also made in two TFE–ethanol mixtures. For each solvolysis, the averages of all the integrated first-order rate coefficients for duplicate runs are listed in Table 1. Specific rates at 50 °C for solvolyses in 80 and 50% ethanol are recorded as footnotes to the table.

Solvolyses of butyl bromide (6)

The specific rates of solvolysis of **6** were determined for five of the solvent compositions: two aqueous ethanol, one aqueous methanol, one aqueous acetone and one aqueous TFE mixture. The average values, determined in the same manner as for the solvolysis of **5**, are listed in Table 1, together with the ratio of the specific rates of solvolysis of **6** relative to solvolysis of **5**.

Examination of the loss of hydrobromic acid in non-aqueous solvents

During studies of HBr production from the solvolysis of **5** in 100% ethanol, 100% methanol and the two TFE–ethanol compositions, it was found that [HBr] rose to a maximum value of considerably less than that which would theoretically have been produced from the [C_4H_7Br]. A similar loss of HCl during fairly slow solvolyses at elevated temperatures of diphenylcarbamoyl chloride in ethanol has recently been reported[22] and the rate of the loss of HCl from an ethanol solution had been studied previously.[23]

The second-order rate coefficients (Table 2) for loss of HBr [eqn. (2)] in the four solvents mentioned above were

$$ROH + HBr \rightleftharpoons RBr + H_2O \qquad (2)$$

Table 2 Second-order rate coefficients[a] for loss of 0.0037 mol dm^{-3} HBr at 70.0 °C and comparison of rates of loss[a] and formation[b] of acid at 20% solvolysis of 0.0035 mol dm^{-3} but-3-enyl bromide (5)

Solvent[c]	$k_2/10^{-4}$ dm^3 mol^{-1} s^{-1} [d]	Rate ratio: acid loss[a]/acid formation[b]
EtOH	11.9 ± 0	0.43
80% EtOH	< 0.001[e]	< 1.2 × 10^{-5}
MeOH[f]	29.0 ± 2.5	0.65
80T-20E	7.5 ± 0.8	0.54
40T-60E	2.78 ± 0.08	0.16

[a] $-d[H^+]/dt = k_2[HBr]^2$. [b] $d[H^+]/dt = k_A[RBr]$, with k_A values from Table 1. [c] Mixed solvents on volume-volume basis at 25.0 °C. [d] Performed in duplicate and average value and standard deviation obtained from a consideration of all of the integrated values. [e] No loss of acid detected and estimated maximum value given. [f] Relatively early equilibrium established ($K = [MeBr]^2/[MeOH_2^+]^2$), with K value of 2.24 ± 0.12.

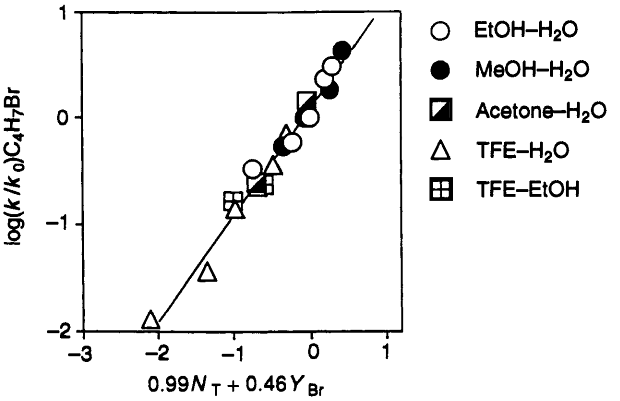

Fig. 1 Plot of log (k/k_o) for solvolysis of but-3-enyl bromide (5) against $lN_T + mY_{Br}$ (using values from Table 1), where l has a value of 0.99 and m has a value of 0.46.

determined after the relatively rapid generation of HBr from the solvolysis of 0.0037 mol dm^{-3} benzyl bromide. The second-order form [eqn. (3)] follows from the rate-determining process

$$-d[H^+]/dt = k_2[HBr^2] \qquad (3)$$

involving nucleophilic attack by bromide ion on the protonated solvent. In methanol, a fairly early equilibrium was established and the equilibrium constant is reported as a footnote to Table 2. It is demonstrated in Table 2 that, at 20% solvolysis of 5, the rate of acid loss is 0.16–0.65 of the rate at which acid is being formed from the solvolysis. No loss of the HBr was observed in 80% ethanol.

The specific rates reported in Table 1 for solvolysis of 5 in the four non-aqueous solvents were obtained in the presence of a slight excess of 2,6-lutidine (2,6-dimethylpyridine), which is capable of acting as a base towards the HBr produced (without interfering with the titration procedure) but is sterically prohibited from competing with the solvent during the substitution reaction of 5.

Discussion

The five comparisons of the specific rates of solvolysis of 5 and 6 at 70 °C (Table 1) indicate in each case a moderately greater rate of solvolysis (by a factor of 1.7 to 2.2) for the saturated 6 relative to the homoallylic 5. This strongly suggests that both substrates are reacting by an identical, presumably S_N2, mechanism over this range of solvents. In contrast, when Servis and Roberts[6] obtained evidence for an S_N1 solvolysis of but-3-enyl tosylate in 98% formic acid, based on extensive rearrangement to ring-containing products, the homoallylic substrate reacted modestly faster than *n*-butyl tosylate.

Simple [eqn. (1), without the lN term] and extended [eqn. (1)] Grunwald–Winstein treatments of the first 19 entries within Table 1 for specific rates of solvolysis of 5 have been carried out. The simple treatment, involving correlation of $\log(k/k_o)$ with Y_{Br} values[16,24] shows essentially no correlation [correlation coefficient (r) of 0.189] with an m value of −0.07 ± 0.09 (probability that the mY_{Br} term is not statistically significant of 0.44) and a c value of −0.27 ± 0.64. The F-test value for the correlation was only 0.63. In contrast, a very good correlation (R = 0.987) is obtained when the full eqn. (1) is used, with correlation against a combination of Y_{Br} and N_T[17] values (Fig. 1). Values are obtained of 0.99 ± 0.04 for l, of 0.46 ± 0.03 for m, of 0.10 ± 0.11 for c and of 297 for the F-test value. The l and m values obtained from the extended Grunwald–Winstein equation treatment are typical of those for an S_N2 solvolysis; for example, the corresponding l and m values for methyl tosylate solvolysis,[20] using N_T and Y_{OTs} scales, are 1.01 and 0.55, respectively.[17a]

Since formic acid decomposes, with a build-up of pressure in sealed tubes, it was considered unwise to attempt a study of the slow reaction at considerably elevated temperature which would have been involved in the formolysis of 5. However, the 97% TFE included in the study (N_T = −3.3; Y_{Br} = 2.5) would be expected to favour S_N1 relative to S_N2 slightly more than the formic acid (N_T = −2.4; Y_{Br} = 2.5), due to the more negative solvent nucleophilicity value. As can be seen in Fig. 1, the 97% TFE lies nicely on the plot and, indeed, its exclusion from the correlation leads essentially to unchanged l, m and c values and slightly reduced R (0.982) and F-test (207) values.

Although, due to the lack of a Y_{Br} value, the specific rate in 90% HFIP was not included in the correlations, one can roughly estimate, from a comparison with Y_{Cl} values,[16] a value of 3.8 for Y_{Br}. In conjunction with the N_T value of −3.84[17a] and the l and m values reported above, one can arrive at a predicted specific rate for S_N2 solvolysis of 5 of 0.16 × 10^{-7} s^{-1}, about one-quarter of the experimental specific rate. This does give some, admittedly only semiquantitative, indication that, in this solvent of higher ionizing power and lower nucleophilicity, there may be a dominant S_N1 component to the solvolysis pathway.

At first glance, it might seem contradictory that, in solvents of similar ionizing power and nucleophilicity, but-3-enyl tosylate reacts primarily by an S_N1 mechanism and the corresponding bromide 5 by an S_N2 mechanism. This is a situation which can be conveniently probed by a consideration of the k_{OTs}/k_{Br} (or k_{OBs}/k_{Br}) rate ratio introduced as a mechanistic tool by Hoffmann.[25] For S_N2 reactions, the value for the ratio varies with nucleophile but it is fairly close to unity, slightly less for attack by powerful nucleophiles and somewhat above for attack by relatively weak nucleophiles, and for S_N1 reactions a much larger value, of around 5000, is usually observed.[25,26]

Bergstrom and Siegel[27] reported specific rates for the ethanolysis of but-3-enyl benzenesulfonate (C_4H_7OBs) at 34.8 and 55.3 °C. Unfortunately an error must have been made in constructing the published table and identical specific rate values are reported for the two temperatures. Fortunately, an extrapolated value at 20 °C is also given and using this in conjunction with the value reported for 34.8 °C (clearly in better agreement with the 20 °C value) leads to an extrapolated specific rate at 70 °C of 9.4 × 10^{-6} s^{-1}; applying the recommended[26] k_{OTs}/k_{OBs} conversion factor of 0.63, one arrives at a calculated value of 5.9 × 10^{-6} s^{-1} for the tosylate. Comparison with the specific rate of ethanolysis of 5 from Table 1 leads to a k_{OTs}/k_{Br} ratio at 70 °C of 12. Giving further support to the belief that the solvolyses of but-3-enyl derivatives in solvents of moderate nucleophilicity and ionizing power are S_N2 in character, this value is virtually identical with k_{OTs}/k_{Br} values[25,28] of 16 and 15 for the corresponding S_N2 ethanolyses of methyl and ethyl tosylates and bromides at 50 °C.

A more challenging situation is presented by a consideration of the mechanism as one moves toward solvents of higher ionizing power and lower nucleophilicity, conditions which increasingly favour the S_N1 pathway in its competition with the S_N2 pathway. Initially, we will concentrate on the formolysis ($N_T = -2.44$; $Y_{Br} = 2.47$) and, using the l, m and c values calculated using eqn. (1) together with the k_o value from Table 1, one can estimate a specific rate for formolysis of **5** at 70 °C of $1.04 \times 10^{-7}\ s^{-1}$. For the corresponding tosylate an experimental value of $3.1 \times 10^{-6}\ s^{-1}$ at 50.3 °C was reported (actually in 98% formic acid)[6] and, assuming that the variation in temperature parallels that for solvolysis in 80% formic acid, a value at 70 °C of $3 \times 10^{-5}\ s^{-1}$ can be obtained, corresponding to a k_{OTs}/k_{Br} ratio of about 300. This value is intermediate between those expected for S_N1 and S_N2 reactions and it reflects a comparison of the S_N1 pathway for the tosylate[6] with the S_N2 pathway for the bromide. If it is further assumed that the k_{OTs}/k_{Br} ratio of 12 for S_N2 reaction in ethanol also applies to the S_N2 reaction in formic acid (there is some supporting evidence in that S_N2 ethanolyses and S_N2 hydrolyses have very similar k_{OTs}/k_{Br} values[25,28]) and that the k_{OTs}/k_{Br} average ratio of about 5000 for S_N1 reactions[26] can be applied to S_N1 formolyses of the but-3-enyl derivatives, we can construct a ladder of relative specific rates of reaction in formic acid at 70 °C. At the bottom will be the S_N1 pathway for the bromide, 17 times faster will be the S_N2 pathway for the bromide, 12 times faster again will be the S_N2 pathway for the tosylate, and finally 25 times faster again will be the S_N1 pathway for the tosylate.

From the S_N1/S_N2 rate ratio of 25 for the tosylate, we can predict that its formolysis will have an approximately 4% component from the S_N2 pathway, in excellent agreement with Kosower's estimate,[18] based on product studies, of a 5–6% component. Based on the calculated value of $1.04 \times 10^{-7}\ s^{-1}$ for the S_N2 specific rate of formolysis of **5**, the corresponding S_N1 value would be 17 times lower at a value of $0.06 \times 10^{-7}\ s^{-1}$. Since the Y_{Br} values are identical for formic acid and 97% TFE, identical specific rates for the S_N1 pathway would be predicted. Based on a correlation using the other 18 solvents ($l = 1.04$, $m = 0.48$, $c = 0.11$), a value for S_N2 solvolysis in 97% TFE of $0.11 \times 10^{-7}\ s^{-1}$ can be calculated, leading to a total ($S_N1 + S_N2$) specific rate of solvolysis in 97% TFE of $0.17 \times 10^{-7}\ s^{-1}$. This value is in excellent agreement with the experimental value (Table 1) of $0.19 \times 10^{-7}\ s^{-1}$ and the analysis indicates an approximately 35% S_N1 contribution to the overall solvolysis rate.

In the present study, the solvent with the greatest tendency toward inducing S_N1 reaction is 90% HFIP ($N_T = -3.84$, $Y_{Br} \approx 3.8$). The predictions here will be more approximate than those previously noted, to a large degree because even the Y_{Br} value is only a rough estimate. The estimated specific rate of S_N1 formolysis of **5** of $0.06 \times 10^{-7}\ s^{-1}$ taken together with the ΔY_{Br} value of about 1.3 and assuming an m value of unity leads to an estimated S_N1 specific rate of solvolysis in 90% HFIP of $1.2 \times 10^{-7}\ s^{-1}$, some 7.5 times larger than the estimated [eqn. (1)] value for S_N2 solvolysis. The total predicted specific rate of $1.36 \times 10^{-7}\ s^{-1}$ for solvolysis in 90% HFIP is a little over twice as large as the experimental (Table 1), but this must be considered as a reasonable agreement considering the several rather drastic approximations involved. The analyses indicate that the minor contribution made by the S_N1 pathway to the overall solvolysis of **5** at 70 °C in 97% TFE becomes the major contributor on moving to 90% HFIP.

Conclusions

The solvolysis of but-3-enyl bromide (**5**) at 70 °C is S_N2 in character over a wide range of solvents: 19 solvents ranging from ethanol ($N_T = 0.37$, $Y_{Br} = -2.4$) to 97% TFE ($N_T = -3.3$, $Y_{Br} = 2.5$). In a simple Grunwald–Winstein treatment, essentially no correlation of $\log(k/k_o)$ with Y_{Br} is observed ($r = 0.189$) but a very good correlation is obtained against a combination of N_T and Y_{Br} when the extended Grunwald–Winstein equation is used ($R = 0.987$). The sensitivity values obtained, 0.99 for l and 0.46 for m, are in excellent accord with the proposed S_N2 mechanism.

Further support for the S_N2 mechanism comes from the observation that the specific rate of solvolysis of butyl bromide (**6**) in five of the solvents is uniformly twice as high as the corresponding specific rate for **5** (suggesting no anchimeric assistance and a modest inductive retardation due to the presence of the double bond) and from the observation for ethanolyses at 70 °C of a k_{OTs}/k_{Br} ratio of 12, essentially identical with ratios which have been reported based on the ethanolyses of methyl and ethyl tosylates and bromides.[25,28]

The extended Grunwald–Winstein equation, as developed, predicts a specific rate by the S_N2 mechanism in 97% TFE which is some 40% lower than the experimental value. Suggesting that this deviation may be meaningful is an estimate of a specific rate of solvolysis of **5** in 97% TFE by the S_N1 mechanism, based on formolysis of but-3-enyl tosylate plus a few reasonable assumptions, of 35% of the experimental specific rate. As one would then expect, there are strong indications that in 90% HFIP ($N_T = -3.8$, $Y_{Br} \approx 3.8$) the S_N1 mechanism becomes predominant.

Although the formolysis of **5** would be well within the range for which S_N2 reaction would be predicted, based on the N_T and Y_{Br} values, previous product studies[6] indicated that about 95% of the formolysis occurred by the S_N1 mechanism when but-3-enyl tosylate was the substrate. We have been able to show in a semiquantitative manner that this is consistent with the large (average value of about 5000) k_{OTs}/k_{Br} value previously established[25,26] as operating for S_N1 reactions. It is possible to predict that the ordering of the four specific rates of formolysis of the tosylate and bromide by the S_N1 or S_N2 mechanism is with the slowest of all being the S_N1 reaction of the bromide, followed by the S_N2 reaction of the bromide, the S_N2 reaction of the tosylate and, fastest of all, the S_N1 reaction of the tosylate. Accordingly, it follows for the formolyses that the dominant pathway for the tosylate will be S_N1 but the dominant pathway for the bromide will be S_N2.

Experimental

Materials

The purifications of acetone,[29] ethanol,[29] methanol,[29] HFIP[30] and TFE[31] were as previously described. Benzyl bromide (Aldrich, 98%), 1-bromobutane (**6**, Aldrich, 99%) and 4-bromobut-1-ene (**5**, Aldrich, 99%) were used as received.

Kinetic procedures

Concentrations of **5** or **6** in the range $3–4 \times 10^{-3}$ mol dm^{-3} were used. For the solvents not containing fluoro alcohol, 5 cm^3 aliquots were removed from 50 cm^3 of solution and, for the fluoro-alcohol-containing solvents, 2 cm^3 portions were removed from 25 cm^3 of solution. Owing to a slow reaction at 70 °C, the runs were carried out in sealed tubes. For all runs, except those in 50% ethanol and the four determinations in a non-aqueous solvent (carried out in the presence of 5×10^{-3} mol dm^{-3} 2,6-lutidine), the time to 10 half-lives was reduced by addition of an equal volume of water to the solution in the tube to be used for the infinity titre. The tubes were removed at appropriate time intervals and cooled in ice–water before being opened and the contents added to 25 cm^3 of acetone containing Lacmoid (resorcinol blue) indicator. The previously produced acid was then titrated with a standardized solution of sodium methoxide in methanol.

For the study of the loss of HBr from solution in a pure alcohol or a TFE–ethanol mixture, the HBr was generated by the relatively rapid solvolysis in the solvent at 70 °C of benzyl bromide. These runs were also performed in sealed tubes. After the maximum amount of acid had been developed, tubes were removed at appropriate time intervals and analysed as indicated above. From the extent of the decrease in acid concentration as a function of time, integrated second-order rate coefficients, according to eqn. 3, were calculated. Values obtained after about 40% reaction (20% for methanolysis) fell off, presumably due to movement toward equilibrium, and only earlier values were averaged to give the values reported in Table 2.

References

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