Solvent Effects on the Solvolysis of *p*-Nitrobenzyl and 3,5-Bis(trifluoromethyl)benzyl *p*-Toluenesulfonates[1)]

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Solvolysis rates of *p*-nitrobenzyl and 3,5-bis(trifluoromethyl)benzyl *p*-toluenesulfonates were determined in a wide variety of solvents. The solvent effects were analyzed based on the Winstein–Grunwald equation. The solvent effect on these deactivated benzyl solvolyses failed to give a single linear correlation with the 2-adamantyl Y_{OTs} parameter. The lower response to the solvent polarity and the pattern of dispersion for respective binary solvent series can be interpreted in terms of nucleophilic solvent assistance. The application of the equation gave a low m value of 0.4 and a large l of close to unity for both derivatives. Furthermore, the l value is also comparable to that for ethyl *p*-toluenesulfonate and even close to that for the methyl derivative, which has generally been defined as the standard $\mathrm{S_N2}$ substrate.

In the previous papers,[2)] we have treated the solvent effects on the solvolyses of benzyl tosylate (*p*-toluenesulfonate) (**1**), a slightly activated *m*-methylbenzyl (**2**) and moderately deactivated *m*-chlorobenzyl (**3**) tosylates, based on the Winstein–Grunwald–Schleyer–Bentley equation;[3,4)]

$$\log(k/k_{80\mathrm{E}}) = mY_{\mathrm{OTs}} + lN_{\mathrm{OTs}}, \qquad (1)$$

where the Y_{OTs} and N_{OTs} are the parameters representing the ionizing power and nucleophilicity of solvents, derived from the solvolyses of 2-adamantyl tosylate and methyl tosylate, respectively.[4)] Equation 1 has most generally been applied to solvolyses of simple aliphatic precursors.[4)] However, we have reported that the solvent effects on the solvolyses of **1**—**3** failed to afford any satisfactory linearity against the conventional Y_{OTs} scale.[2)] The benzylic $\mathrm{S_N1}$ solvolyses very often showed significant dispersal of the mY plot for different binary solvent mixture series, resulting in a rather low m value.[3a,3d,5—9)] We have also observed the significant dispersion of Y_{OTs} plots for binary aqueous solvent series, in many solvolyses, such as α-(*t*-butyl)benzyl solvolysis,[10)] neophyl (2-methyl-2-phenylpropyl) and the related β-aryl-assisted solvolyses,[11,12)] and α-(*p*-methoxyphenyl)vinyl solvolyses.[13)] All these solvolyses are likely to be nucleophilically limiting, and hence the dispersed solvent effect plots should be ascribed to the inadequacy of the conventional Y_{OTs} parameter in accounting for the polarity-dependence of benzylic systems. The dispersion of the Y_{OTs} plots among various series of aqueous binary solvent mixtures was not attributed to the solvent nucleophilicity, but rather to certain other factors associated with the benzylic $\mathrm{S_N1}$ ionization process. There are significant differences in solvation between aryl and alkyl substrates. Through the π-delocalization, the local cationic charge at the reaction site can be transferred effectively into the aryl ring at the transition state.

The ring-substituent effect on the benzyl solvolysis indicates a spectrum of behavior between $\mathrm{S_N1}$ and $\mathrm{S_N2}$ for a range of substituted benzyl series;[14)] there is a gradual change in mechanism for a series of substituted benzyl tosylates from the limiting $\mathrm{S_N1}$ mechanism for strongly electron-donating substituents, possibly through the so-called $\mathrm{S_N2}$ (intermediate) mechanism[4,15)] for moderately donating substituents, to the classical $\mathrm{S_N2}$ mechanism for a range of electron-withdrawing substituents. The solvolysis of substituted benzyl tosylates will be suitable as a model system to examine the validity of the Bentley–Schleyer method of continuous $\mathrm{S_N2}$–$\mathrm{S_N1}$ mechanisms.[4)]

The solvolyses of moderately activated benzyl substrates as well as the parent unsubstituted benzyl tosylate were in fact not satisfactorily correlated by a conventional solvent polarity scale Y_{OTs}. With appropriate choice of a reference Y_{Bz} scale, Winstein–Grunwald profiles of solvent effects provide quantitative dissections of the $\mathrm{S_N1}$ and $\mathrm{S_N2}$ characters of the transition states.[2)] The neighboring aryl group in the anchimeric assistance mechanism plays the role of an intramolecular nucleophile which displaces the leaving group from the rear-side of the reaction center, and the solvent polarity parameter Y_{Δ} or Y_{neo} based thereon should best be referred to the polarity-dependence of the transition state of a concerted S_N2 solvolysis. The involvement of the solvent nucleophilicity can then be recognized readily as a deviation from the expected behavior.

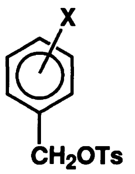
The use of such an appropriate Y scale will enable us to examine the real validity of N_{OTs} parameters for benzylic solvolyses. However, Schleyer and Bentley found difficulties in describing the involvement of solvent nucleophilicity even in the solvolyses of simple secondary alkyl tosylates.[4,15] Kevill introduced a set of nucleophilicity parameters, N_{KL}, based on the triethyloxonium ion solvolysis and demonstrated better correlations (Eq. 1) for the solvolysis of substituted benzyl tosylates with N_{KL} than with the conventional N_{OTs} parameter.[16]

In order to confirm the validity of the N_{OTs} parameter, more detailed examination would be necessary for solvent effects on the solvolyses of strongly deactivated benzyl tosylates carrying electron-withdrawing substituents. Accordingly, extensive studies were carried out concerning the substituent-dependence of the solvent effect in the S_N2 reaction of deactivated benzyl tosylates. We have determined the solvolysis rates of *p*-nitrobenzyl (**4**) and 3,5-bis(trifluoromethyl)benzyl (**5**) tosylates in an extended range of solvents (Chart 1), and analyzed the solvent effects in terms of the Winstein–Grunwald Equation, in comparison with those for activated benzyl derivatives.

Results

Solvolysis rates of **4** and **5** were determined in a wide variety of solvents; such as aqueous binary solvent mixtures of ethanol, methanol, acetone, acetonitrile, 2,2,2-trifluoroethanol (TFE), and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), and acetic acid–formic acid (AF) and ethanol–TFE mixtures (ET). The rate measurements were carried out in aqueous organic solvents mostly by a conductimetric method and in organic acids by the ordinary titrimetric method. The kinetic results are listed in Tables 1 and 2, together with relevant activation parameters. Solvolysis rates of ethyl and methyl tosylates were also determined for comparison with those of deactivated benzyl tosylates and are summarized in Tables 3 and 4.

As shown in Tables 1 and 2, solvolysis of **4** was only about two times faster than that of **5** for a wide range of solvents. Further the entropies of activation for these benzyl solvolyses are typical of the S_N2 solvolyses, which are in the same range as those of ethyl tosylate given in Table 3.



1 : X = H

2 : X = *m*-CH$_3$

3 : X = *m*-Cl

4 : X = *p*-NO$_2$

5 : X = 3,5-(CF$_3$)$_2$

Chart 1.

In Fig. 1, the solvolysis rates of **4** at 45 °C are plotted, in a logarithmic scale, against the 2-adamantyl-based Y_{OTs} which were determined previously.[2] No simple linear mY relationship is observed for the solvolysis of any deactivated benzyl tosylate. Points for aqueous ethanol (EW), aqueous methanol (MW), and aqueous acetone (AW) solvents fall on separate lines of different slopes ($m_{EW}=0.32$ for aq ethanol series and $m_{AW}=0.45$ for aq acetone series) with a significant gap (0.55 log-unit at $Y_{OTs}=0$), and in particular the plots for less nucleophilic solvents, acids and fluorinated alcohols, lie far below the aq alcoholic and acetone lines. The m value distinctly lower than unity expected for the S_N1 reaction as well as the characteristic deviation pattern of the mY_{OTs} plots of little or non-nucleophilic solvents in the decelerating direction is consistent with the previous interpretation[3b,4,14,16] in terms of the extensive involvement of solvent nucleophilicity.

Logarithmic rates of solvolysis of **5** exhibited a dispersion pattern of the Y_{OTs} plot quite similar to that of **4** in Fig. 1. Furthermore, there is an important linear log–log relationship with a unit slope between these two solvolyses. This simple linearity with an excellent precision of $R=0.997$ and SD$=\pm0.06$ for $n=33$ is just what can be expected for the identical relative contributions from the solvent nucleophilicity to the solvolyses of *p*-nitro **4** and 3,5-bistrifluoromethyl **5** derivatives.

$$\log(k/k_{80E})_{\mathbf{4}} = 1.02\ \log(k/k_{80E})_{\mathbf{5}} + 0.028. \tag{2}$$

The mY_{OTs} plots for both **4** and **5** exhibit a very similar pattern to those of typical S_N2 substrates such as methyl and ethyl tosylates.[17] A fairly good linear correlation ($R=0.974$ and SD$=\pm0.18$) was given for **4** against $\log(k/k_{80E})$ of methyl tosylate in Fig. 2. Furthermore, by taking account of slightly different responses to the solvent polarity between solvolyses of methyl tosylate and this benzyl tosylate, a moderately improved correlation ($R=0.989$ and SD$=\pm0.12$) can be obtained.

$$\log(k/k_{80E})_{\mathbf{4}} = 0.96\ \log(k/k_{80E})_{MeOTs} + 0.11Y_{OTs} - 0.03. \tag{3}$$

It is also worth noting that there are even better direct linear relationships against ethyl tosylate with a slope of essentially unity for both **4** and **5**.

$$\log(k/k_{80E})_{\mathbf{4}} = 1.11\ \log(k/k_{80E})_{EtOTs} - 0.04 \quad (R = 0.993,\ \mathrm{SD} = \pm0.08), \tag{4}$$

$$\log(k/k_{80E})_{\mathbf{5}} = 1.08\ \log(k/k_{80E})_{EtOTs} - 0.07 \quad (R = 0.984,\ \mathrm{SD} = \pm0.13). \tag{5}$$

Correlation Analysis. It is highly likely that those benzyl substrates carrying strongly deactivating ring substituents react by an S_N2 mechanism,[14] and

Table 1. Rate Data for Solvolysis of *p*-Nitrobenzyl Tosylate[a]

Solv.[b]	$10^5\ k/\mathrm{s}^{-1}$	$10^5\ k/\mathrm{s}^{-1}$ (Temp/°C)	$\Delta H^{\ddagger}_{45\,^{\circ}\mathrm{C}}$[c]	$\Delta S^{\ddagger}_{45\,^{\circ}\mathrm{C}}$[c]
	45 °C		kcal mol^{-1}	e.u.
30E	48.08	6.934(25)	17.6	−18.5
40E	29.04	4.137(25), 69.18(55)	17.6	−19.4
50E	18.31	2.457(25), 43.92(55)	18.1	−18.9
60E	13.19	1.831(25), 33.18(55)	18.1	−19.5
70E	10.06	3.799(35)	18.3	−19.3
80E	7.322	2.730(35), 17.81(55)	18.2	−20.4
90E	4.777	1.687(35), 11.63(55)	18.8	−19.5
EtOH	1.816			
50M	39.08			
60M	27.15			
80M	12.62			
MeOH	4.185	0.5271(25)	18.9	−19.3
20A	49.46			
30A	24.94	3.719(25)	17.3	−20.8
40A	12.64	1.732(25)	18.1	−19.6
50A	6.307			
60A	3.191			
70A	1.763			
80A	0.7694	0.285(35),[d] 1.93(55)[d]	18.6	−23.7
50AN	4.597			
60AN	2.578			
80AN	0.6837			
90AN	0.1609[e]	0.4041(55), 2.175(75)	18.5	−27.1
30T	8.625	22.78(55)	19.5	−15.9
40T	4.487	1.503(35), 11.94(55)	20.2	−15.1
50T	2.743	7.308(55)	19.7	−17.6
80T	0.4466[d]	6.759(75)[d]	19.3	−22.5
97Tw	0.08687[e]	0.4997(65),[f] 1.091(75), 6.710(100)[f]	18.0	−29.8
80ET	1.999			
60ET	1.505			
40ET	1.044			
20ET	0.5155			
AcOH[d]	0.02204[e]	0.480(75), 13.92(115)	22.0	−20.1
50AF	0.325			
HCOOH[d]	1.071			

a) Conductimetrically determined, unless otherwise noted. b) Volume percent (v/v) of first-named organic component of mixed aqueous solvent, unless otherwise noted. Abbreviation; E=ethanol, M=methanol, A=acetone, AN=acetonitrile, T=TFE=2,2,2-trifluoroethanol, 50AF=50 : 50 (v/v) acetic acid–formic acid mixture, and ET=ethanol–TFE (e.g., 80ET=80 : 20 (v/v) EtOH–TFE mixture). Suffix w means weight percent (w/w). c) 1 cal=4.184 J. d) Titrimetrically determined. e) Extrapolated from rate data at other temperatures. f) The ampoule technique with conductivity determination.

therefore no direct linearity against any Y scale could be expected for the solvolysis of either **4** or **5**. The pattern of deviations of the plot as well as the lower response to the solvent polarity can reasonably be accounted for by the predominant involvement of solvent nucleophilicity. By statistical analysis with Eq. 1, including the lN_{OTs} term, the solvent nucleophilicity accounts for the nonlinearity. The results are summarized in Table 5.

For the total solvent set, direct treatment with the conventional Y_{OTs} parameter gives no linear correlation at all, as shown in Fig. 1, but the dual parameter treatments by Eq. 1 involving the nucleophilicity term give an improved correlation as shown in Fig. 3, giving $m=0.40$ and $l=0.94$ for **4** (Entry 1 of Table 5). The solvolysis of **5** was also analyzed in the same manner to give results (Entry 5) quite analogous to those for **4** with a comparable precision. The response to the solvent nucleophilicity, l value, remains the same for both of these benzyl tosylates. Furthermore, the l value is also comparable to that for ethyl tosylate (Entry 9) and even closer to that for methyl tosylate (Entry 13) which has generally been defined as the standard $\mathrm{S_N2}$ substrate.

The previous studies showed that the polarity scale Y_{Bz} based on the solvolysis of either neophyl tosylate (Y_{neo}) or α-(*t*-butyl)benzyl tosylate ($Y_{\alpha\text{-Bu}}$) ap-

Table 2. Rate Data for Solvolysis of 3,5-Bis(trifluoromethyl)benzyl Tosylate[a]

Solv.[b]	$10^5\ k/\mathrm{s}^{-1}$ 45 °C	$10^5\ k/\mathrm{s}^{-1}$ (Temp/°C)	$\Delta H^{\ddagger}_{45\ ^\circ\mathrm{C}}$[c] kcal mol^{-1}	$\Delta S^{\ddagger}_{45\ ^\circ\mathrm{C}}$[c] e.u.
30E	26.40	133.4(65), 259.7(75)	16.2	−24.0
40E	15.49	85.15(65), 172.7(75)	17.1	−22.2
50E	10.53	122.1(75)	17.3	−22.3
60E	7.805			
70E	5.878			
80E	4.407	52.43(75)	17.5	−23.5
90E	2.934	34.95(75)	17.5	−24.3
EtOH	1.099	7.062(65), 15.64(75)	18.9	−21.9
50M	23.88			
60M	16.78			
80M	7.957			
MeOH	2.955			
30A	13.00	1.822(25)	17.9	−20.2
40A	6.446			
50A	3.375			
60A	1.780			
70A	0.9393			
80A	0.4772[d]	6.833(75)[d]	18.9	−23.6
50AN	2.322			
60AN	1.389			
80AN	0.4141			
90AN	0.1128[e]	0.2853(55), 0.6490(65), 1.520(75)	18.3	−28.2
30T	3.072	23.61(65), 55.77(75)	20.7	−14.2
40T	1.961	32.90(75)	20.1	−17.2
50T	1.294	21.49(75)	20.0	−18.2
80T	0.3539[d]	5.184(75)[d]	19.1	−23.7
97Tw	0.0503[e]	0.2803(65),[d] 3.638(100)[d]	17.7	−31.8
80ET	1.324			
60ET	0.9673			
40ET	0.6284			
20ET	0.2728			
50HFIP[f]	0.3521			
97HFIPw[g]	0.009311[e]	0.1268(75),[d] 0.8108(100)[d]	18.5	−32.6
AcOH[h]	0.0131[e]	0.2889(75), 8.498(115)	22.1	−20.8
HCOOH[h]	0.5877			

a)b)c) See footnotes a, b, and c of Table 1. d) See footnote f of Table 1. e) See footnote e of Table 1. f) 50(v/v)% aqueous 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). g) 97(w/w)% aqueous HFIP. h) See footnote d of Table 1.

peared particularly suitable for the solvolyses of benzyl tosylates.[2] For the electron-donating derivatives which solvolyze mainly by the $\mathrm{S_N1}$ mechanism, we obtained appreciably improved correlations with Eq. 6 using the $\log k$ values of neophyl tosylate as a reference Y_{Bz} instead of the 2-adamantyl-based Y_{OTs}.[2]

$$\log(k/k_{80\mathrm{E}}) = mY_{\mathrm{Bz}} + lN_{\mathrm{OTs}}. \qquad (6)$$

Thus the present $\mathrm{S_N2}$ solvolyses were treated with Eq. 6 using various Y_{Bz} scales determined on the basis of nucleophilically limiting benzylic solvolyses; $Y_{\alpha\text{-Bu}} = \log(k/k_{80\mathrm{E}})_{\alpha\text{-}(t\text{-Butyl})\text{benzyl OTs}}$, $Y_{\mathrm{neo}} = \log(k/k_{80\mathrm{E}})_{\text{Neophyl OTs}}$, and $Y_{\Delta} = \log(k/k_{80\mathrm{E}})_{p\text{-Methoxyneophyl OTs}}$. The correlation results with Eq. 6 using various Y_{Bz} are compared with those by Eq. 1 using Y_{OTs} in Table 5. Either $Y_{\alpha\text{-Bu}}$ or Y_{neo} parameter was applied to the substituted benzyl derivatives **4** and **5**, in nearly the same precision as that with conventional Y_{OTs}. The results in Table 5 appear to present a common set of solvent nucleophilicity for benzyl tosylates and simple alkyl $\mathrm{S_N2}$ substrates, ethyl and methyl tosylates. It may also be concluded that all these solvent polarity Y_{Bz} scales can be nearly equally applicable to the solvolyses of these deactivated benzyl tosylates. We find virtually identical l values with identical precision (i.e., correlation coefficients of about 0.99), for all the correlations involving either **4** or **5** with $Y_{\alpha\text{-Bu}}$ and Y_{neo} (and/or Y_{Δ}) scale as well as Y_{OTs}.

Discussion

The m values for all the present deactivated benzyl precursors were found to be significantly smaller than the value of unity expected for the limiting $\mathrm{S_N1}$ mech-

Table 3. Rate Data for Solvolysis of Ethyl Tosylate[a)]

Solv.[b)]	$10^5\ k/\mathrm{s}^{-1}$ 45 °C	$10^5\ k/\mathrm{s}^{-1}$ (Temp/°C)	$\Delta H^{\ddagger}_{45\,°\mathrm{C}}$[c)] kcal mol^{-1}	$\Delta S^{\ddagger}_{45\,°\mathrm{C}}$[c)] e.u.
30E	2.785			
40E	1.777			
50E	1.345	2.18(50),[e,f)]		
60E	1.038	2.767(55), 17.60(75)	20.2	−18.1
70E	0.7658[d)]	2.115(55), 13.54(75)	20.4	−17.8
80E	0.5571[d)]	1.541(55), 9.893(75) 0.923(50)[e,f)]	20.5	−18.4
90E	0.3838[d)]	1.063(55), 6.840(75)	20.5	−19.0
EtOH	0.1831[d)]	0.5183(55), 3.471(75) 0.246(50),[e,f)] 2.98(75)[e,g)]	21.0	−19.1
50M	2.112			
60M	1.410			
80M	0.8100			
MeOH	0.3871	0.483(50)[e,f)]		
30A	1.822			
40A	1.027			
50A	0.5936			
60A	0.3405			
70A	0.1826			
80A	0.08282			
50AN	0.5364[d)]	1.425(55), 8.498(75)	19.6	−21.1
60AN	0.2762[d)]	0.7949(55), 5.487(75)	21.3	−17.2
50D[h)]	0.6805			
60D[h)]	0.3766			
80D[h)]	0.1024[d)]	0.3071(55), 2.285(75)	22.1	−16.5
30T	1.032			
40T	0.5212			
50T	0.2247			
80T	0.04951[d)]	0.1468(55), 1.070(75)	21.9	−18.6
80ET	0.1991[d)]	0.5486(55), 3.497(75)	20.4	−20.6
AcOH[e)]	0.00254[d,g)]	0.0739(74.56),[g)] 0.847(99.63)[g)] 0.00383(50),[f)] 1.06(100),[i)] 2.43(110),[i)] 3.56(115),[i)] 5.64(120)[i)]	24.4	−16.6
HCOOH[e)]	0.0844[d,g)]	0.431(60.05),[g)] 1.85(74.75)[g)]	22.2	−16.7
TFA[j)]	0.00105[d)]	0.0226(75), 0.204(100), 1.35(125)	21.9	−26.3

a)b)c) See footnotes a, b, and c of Table 1. d) Extrapolated from rate data at other temperatures. e) Titrimetrically determined. f) Ref. 3b g) S. Winstein and H. Marshall, *J. Am. Chem. Soc.*, **74**, 1120 (1952). h) Aqueous dioxane. i) W. Pritzkow and K. H. Schöppler, *Chem. Ber.*, **95**, 834 (1962). j) I. L. Reich, A. Diaz, and S. Winstein, *J. Am. Chem. Soc.*, **91**, 5635 (1969) (spectrophotometrically determined).

anism. There also are remarkable dispersions among various binary aqueous solvent series, in the solvolysis of deactivated substrates where nucleophilic solvent assistance is inevitable, and no direct linearity against the 2-adamantyl-based Y_{OTs}, accompanied by substantial downward deviations for solvents of low nucleophilicity. Marked improvement in the linearity can in fact be brought about for Eq. 1 by including the lN term for the solvent nucleophilicity. Nevertheless, it should be particularly noted that the Bentley–Schleyer treatment with Eq. 1 based on the Y_{OTs} and N_{OTs} parameters does not appear to be capable of achieving an exact single linear correlation for the benzyl solvolysis.[2)] We have already pointed out that there is different dispersion behavior in the solvent effect on $\mathrm{S_N}1$ solvolyses of benzyl substrates and 2-adamantyl tosylate, or those of aryl-substituted and simple alkyl substrates, and, of course, all the apparent dispersion cannot simply be attributed to the nucleophilic solvent assistance.[2,11—13)]

It is apparent in Table 5 that the precision of the correlation (with Eq. 6) of activated substrated **1**—**3** (Entries 17—28) depends significantly upon the choice of Y_{Bz} parameters, whereas in the case of deactivated **4** and **5** (Entries 1—8) the goodness of the fit appears insensitive to the choice of Y_{Bz} scale. The dispersion behavior of the mY correlation for solvent series observed for the activated benzyl substrates is no longer significant for these strongly deactivated substrates. The im-

Table 4. Solvolysis Rates of Methyl Tosylate[a]

Solv.[b]	10^5 k/s^{-1} 50 °C	10^5 k/s^{-1} (Temp/°C)
20E	10.0	
30E	6.78	4.179(45)
40E	5.28	3.038(45)
50E	4.270, 4.41[c,d]	2.614(45)
	5.52[f,g]	43.7(74.9),[f] 268(100)[f]
60E	3.519, 4.43[f,g]	2.106(45), 35.3(75),[f] 214(100)[f]
70E	2.917	1.714(45)
80E	2.253, 2.22[c,d]	1.331(45)
90E	1.584, 1.69[e,f]	0.9552(45), 15.4(75),[f] 104(100)[f]
EtOH	0.7411, 0.655[c,d]	0.4364(45), 4.51(70),[d] 6.87(75.01)[e]
50M	5.946	3.508(45)
60M	4.635	2.781(45)
80M	2.786	1.669(45)
MeOH	1.22	0.1197(30),[d] 0.675(45), 3.68(62.5)[d]
	1.06[c,d,g]	0.363(40),[d] 7.37(70),[d] 17.67(80)[d]
i-PrOH	0.477, 0.414[c,h]	
20A	6.63	
30A	4.68	2.905(45)
40A	3.01	1.881(45)
50A	2.101	1.248(45)
60A	1.315	0.7482(45)
70A	0.7692	0.4346(45)
80A	0.3663	0.2363(45)
50AN	1.475[g]	0.8792(45), 2.440(55), 6.313(65)
60AN	0.9463[g]	0.5795(45), 1.521(55), 3.790(65)
80AN	0.2797[g]	0.1725(45), 0.4394(55), 1.140(65) 2.556(75)
90AN	0.07295[g]	0.1188(55), 0.3060(65), 0.7340(75)
50D[j]	2.426[i]	1.456(45)
60D[j]	1.476	0.8759(45)
80D[j]	0.5263[i]	0.3018(45)
30T	1.91	
40T	1.27	
50Tw	1.13[g,k]	12.2(74.9),[k] 96.1(99.7)[k]
50T	0.717	
70Tw	0.564,[g,k] 0.440[l]	4.34(74.8),[k] 25.9(99.8)[k]
80T	0.0823[g,k]	9.32(99.7),[k] 1.14(75.85)[k]
	0.106[g]	0.474(65), 4.35(90)
97Tw	0.0128[g,k]	5.38(124.7),[k] 0.935(99.8)[k]
TFE	0.0064,[l] 0.0076[c,k]	
50HFIP	0.208	
97HFIPw	0.00144[c,g]	0.0351(75.2),[c] 0.207(89.22),[c] 0.549(100.01)[c]
80ET	0.63[m]	
60ET	0.463[l]	
40ET	0.248[l]	
20ET	0.083[m]	
AcOH	0.00632[e,g]	0.0852(75.01),[e] 0.786(99.6)[e]
HCOOH	0.083[e,g]	1.06(75.01)[e]
TFA[n]	0.000143[g]	0.113(125), 0.0164(100)

a) Conductimetrically determined. b) Footnote b of Table 1. c) Ref. 4. d) R. E. Robertson, *Can. J. Chem.*, **31**, 589 (1953). e) Footnote g of Table 3. f) D. J. Raber, W. C. Neal, Jr., M. D. Dukes, J. M. Harris, and D. L. Mount, *J. Am. Chem. Soc.*, **100**, 8137 (1978). g) Extrapolated from rate constants at other temperatures. h) J. B. Hyne and R. E. Robertson, *Can. J. Chem.*, **34**, 863 (1956). i) Estimated from linear logarithmic rates relation between 50 and 45 °C. j) Aqueous dioxane. k) D. J. Raber, M. D. Dukes, and J. Gregory, *Tetrahedron Lett.*, **1974**, 667. l) J. Kaspi and Z. Rappoport, *J. Am. Chem. Soc.*, **102**, 3829 (1980). m) D. A. da Roza, L. J. Andrews, and R. M. Keefer, *J. Am. Chem. Soc.*, **95**, 7003 (1973). n) Footnote j of Table 3.

provement of precision of the correlation of Eq. 6 by using Y_{neo} in place of Y_{OTs} is significant for activated derivatives, but becomes less significant or even insignificant as the substituent becomes electron-withdrawing. It is evident that the deviation from the correlation depends largely on the mY term rather than on the lN

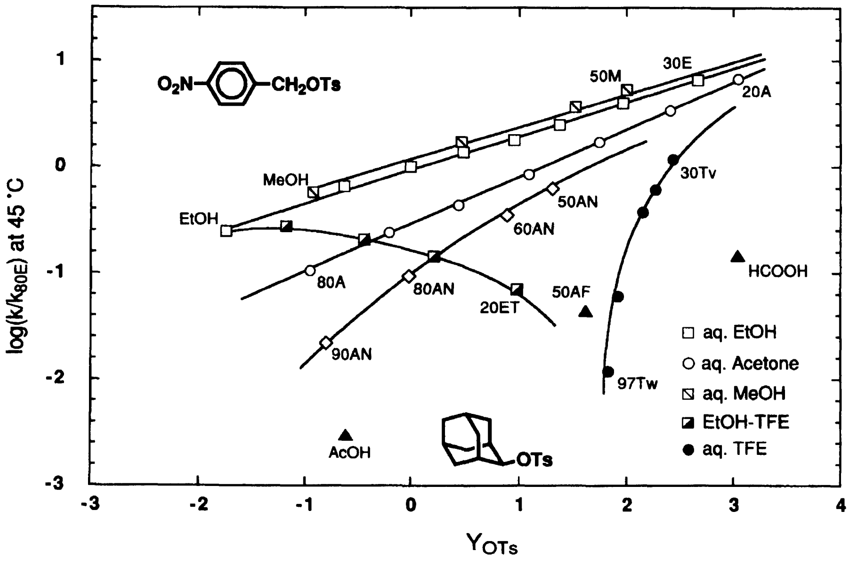


Fig. 1. The mY_{OTs} plots for solvolysis of *p*-nitrobenzyl tosylate.

Table 5. Correlation Analysis by Eq. 6 with Y_{OTs}, $Y_{\alpha\text{-Bu}}$, Y_{neo}, and Y_{Δ}

No.	System	$Y^{a)}$	m	l	c	$R^{b)}$	$SD^{c)}$	$n^{d)}$
1	*p*-Nitrobenzyl	Y_{OTs}	0.40±0.02	0.94±0.03	−0.04	0.987	±0.13	35
2	(45 °C)	$Y_{\alpha\text{-Bu}}$	0.44±0.02	0.98±0.03	−0.07	0.992	±0.10	34
3		Y_{neo}	0.62±0.03	0.99±0.03	0.04	0.989	±0.12	35
4		Y_{Δ}	0.79±0.04	1.03±0.03	0.08	0.987	±0.13	35
5	3,5-$(CF_3)_2$benzyl	Y_{OTs}	0.36±0.02	0.94±0.03	−0.04	0.983	±0.16	35
6	(45 °C)	$Y_{\alpha\text{-Bu}}$	0.39±0.02	0.99±0.03	−0.06	0.986	±0.14	35
7		Y_{neo}	0.56±0.03	0.99±0.03	0.04	0.985	±0.15	35
8		Y_{Δ}	0.71±0.04	1.01±0.03	0.05	0.985	±0.15	35
9	Ethyl	Y_{OTs}	0.35±0.02	0.81±0.02	−0.02	0.991	±0.10	31
10	(45 °C)	$Y_{\alpha\text{-Bu}}$	0.38±0.01	0.88±0.02	−0.01	0.994	±0.07	30
11		Y_{neo}	0.57±0.02	0.89±0.02	0.07	0.994	±0.09	31
12		Y_{Δ}	0.70±0.03	0.94±0.03	0.11	0.988	±0.10	30
13	Methyl	Y_{OTs}	0.30	1.00	(Definition)			
14	(50 °C)	$Y_{\alpha\text{-Bu}}$	0.32±0.01	1.04±0.01	0.00	0.997	±0.07	42
15		Y_{neo}	0.46±0.02	1.06±0.02	0.08	0.995	±0.10	45
16		Y_{Δ}	0.58±0.03	1.06±0.02	0.09	0.991	±0.12	44
17	*m*-Chlorobenzyl	Y_{OTs}	0.51±0.03	0.61±0.05	−0.15	0.933	±0.28	42
18	(25 °C)	$Y_{\alpha\text{-Bu}}$	0.57±0.03	0.69±0.04	−0.16	0.966	±0.20	42
19		Y_{neo}	0.84±0.04	0.72±0.04	−0.03	0.970	±0.19	42
20		Y_{Δ}	1.07±0.05	0.75±0.04	0.00	0.969	±0.19	42
21	Benzyl	Y_{OTs}	0.67±0.04	0.36±0.06	−0.16	0.939	±0.33	42
22	(25 °C)	$Y_{\alpha\text{-Bu}}$	0.75±0.03	0.46±0.04	−0.17	0.972	±0.22	42
23		Y_{neo}	1.11±0.04	0.50±0.04	−0.01	0.980	±0.19	42
24		Y_{Δ}	1.41±0.05	0.54±0.04	0.03	0.976	±0.21	42
25	*m*-Methylbenzyl	Y_{OTs}	0.72±0.05	0.27±0.06	−0.16	0.937	±0.35	41
26	(25 °C)	$Y_{\alpha\text{-Bu}}$	0.80±0.03	0.39±0.04	−0.17	0.973	±0.24	41
27		Y_{neo}	1.19±0.04	0.43±0.04	0.00	0.983	±0.19	41
28		Y_{Δ}	1.50±0.05	0.46±0.04	0.04	0.979	±0.21	41

a) $\log(k/k_{80E}) = mY_{Bz} + lN_{OTs} + c$. $Y_{\alpha\text{-Bu}} = \log(k/k_{80E})_{\alpha\text{-}(t\text{-Butyl})\text{benzyl OTs}}$, $Y_{neo} = \log(k/k_{80E})_{\text{Neophyl OTs}}$, and $Y_{\Delta} = \log(k/k_{80E})_{p\text{-Methoxyneophyl OTs}}$. Y_{Bz} values were taken from Ref. 2. b) Correlation coefficient. c) Standard deviation. d) Number of data points involved.

term. The precision of correlation of these deactivated substrates should depend upon the linearity of the nucleophilicity term, or the validity of N_{OTs} values.

Kevill demonstrated that the use of a set of nucleophilicity parameters, N_{KL} (derived from the solvolysis of triethyloxonium ion), gives a better correlation of solvent effects in various solvolyses than the conventional N_{OTs} parameters.[16] Improved correlations with Eq. 1 were reported for the solvolysis of substituted benzyl tosylates, by using the N_{KL} instead of the N_{OTs}

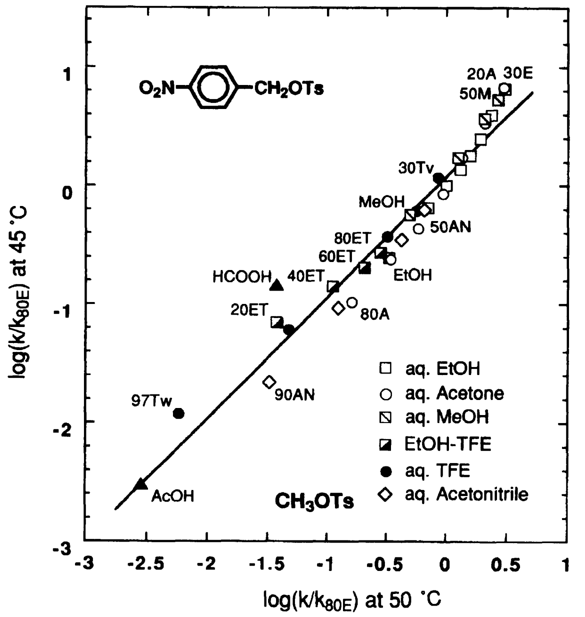


Fig. 2. Linear logarithmic rates relation between solvolyses of *p*-nitrobenzyl and methyl tosylates.

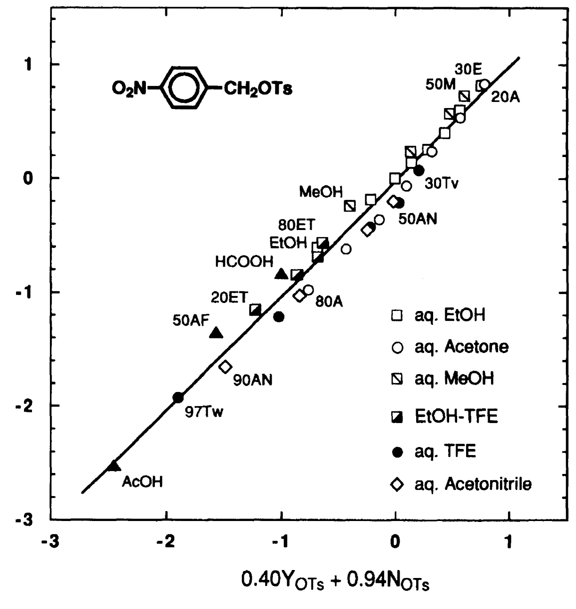


Fig. 3. The ($mY_{\mathrm{OTs}}+lN_{\mathrm{OTs}}$) plots for solvolysis of *p*-nitrobenzyl tosylate.

parameter.[16b)] We also achieved appreciably improved results using the N_{KL} scale for the moderately activated benzyl tosylates **1** and **2**, to lend some support for Kevill's conclusion.[2)] Nevertheless, the number of rate data involved in those analyses is small and the precision of the fit of the Kevill treatment also does not exceed the precision of our correlation results with Eq. 6 using the N_{OTs}, as is found in Table 5. Thus the better results with the Kevill modification do not immediately imply the inadequacy of N_{OTs} parameter values based on methyl tosylate solvolysis. It is therefore worth noting that the solvolysis of ethyl tosylate shows better correlations with $Y_{\alpha\text{-Bu}}$ (and/or Y_{neo}) than with Y_{OTs} in Eq. 6, even though it would be dangerous to place confidence in much smaller variations of precision parameters.

The nucleophilic solvent assistance (lN term) in these deactivated substrates can be separated as the quantity; $\log(k/k_{80\mathrm{E}})-mY_{\mathrm{Bz}}$. Because the response of these substrates to the solvent polarity is nearly as low as the m value of 0.3 assigned for methyl tosylate of $\mathrm{S_N2}$ mechanism, the extent of the mechanistic involvement of solvent nucleophilicity can be rather accurately estimated, regardless of the different Y_{Bz} scales employed. There is indeed a strict linearity ($R=0.997$) between the nucleophilicity quantities for **4** and **5**.

$$\log(k/k_{80\mathrm{E}})_5 - 0.36Y_{\mathrm{OTs}} = 0.99(\log(k/k_{80\mathrm{E}})_4 - 0.40Y_{\mathrm{OTs}}) + 0.0001. \quad (7)$$

The result clearly suggests that the nucleophilicity quantity in the *p*-nitrobenzyl solvolysis **4** can be utilized as a reference N scale in place of N_{OTs} in Eq. 6. Furthermore, for the correlation of benzylic solvolyses, it is statistically even more accurate to apply the $\log(k/k_{80\mathrm{E}})$ of **4** directly as the N scale without dissection in the modified form,

$$\log(k/k_{80\mathrm{E}}) = mY_{\mathrm{Bz}} + lN_{\mathrm{Bz}}, \quad (8)$$

where N_{Bz} corresponds to the $\log(k/k_{80\mathrm{E}})_4$, denoted $N_{p\text{-}\mathrm{NO_2}}$, for the solvolysis of **4**.

Equation 8 is applied to the solvolyses of **3** and unsubstituted **1** as summarized in Table 6. For the *m*-chloro derivative **3**, the $N_{p\text{-}\mathrm{NO_2}}$-based correlations (Eq. 8) are all appreciably better, irrespective of the Y_{Bz} scale utilized, than the corresponding correlations with Eq. 6 using N_{OTs} (Table 5), and the same is also true for the correlation of the solvolysis of **1**. In all the cases, the Y_{Bz} scale based on either neophyl (Y_{neo}) or *p*-methoxyneophyl solvolysis (Y_{Δ}) is appreciably more suitable to the benzyl solvolyses than the conventional Y_{OTs} scale. Nevertheless, the correlations with Eq. 8 for all these derivatives are still not entirely satisfactory. Kevill already discussed the inadequacy of the m value assigned for the methyl solvolysis on which the conventional N_{OTs} scale is based.[16)] When a pair of the standard Y_{OTs} and N_{OTs} parameters are employed as in Eq. 1, the uncertainty of the m value of the methyl tosylate correlation defining the N_{OTs} scale should not affect the precision of the correlation.[17)] On the other hand, use of any Y scales other than the standard Y_{OTs} combined with N_{OTs} should involve some deviation due to a substantial discrepancy arising from the definition. Nevertheless, the correlation with the standard Y_{OTs} is evidently not better than those with other Y_{Bz} scales. The inadequacy of Y_{OTs} scale is certainly responsible for the deviation from the expected behavior of the benzylic solvent effect. It is therefore all the more remarkable that the correlation for **3** with Eq. 8 using the

Table 6. Correlation Analysis by Eq. 8 with N_{Bz}

No.	System	mY_{Bz}	lN_{Bz}[a)]	c	R[b)]	SD[c)]	n[d)]
1.	Benzyl	$0.49Y_{\mathrm{OTs}}$	$0.53N_{p\text{-}\mathrm{NO_2}}$	−0.08	0.961	±0.27	35
		$0.55Y_{\alpha\text{-}\mathrm{Bu}}$	$0.53N_{p\text{-}\mathrm{NO_2}}$	−0.15	0.981	±0.19	35
		$0.77Y_{\mathrm{neo}}$	$0.55N_{p\text{-}\mathrm{NO_2}}$	0.00	0.986	±0.16	35
		$0.96Y_{\Delta}$	$0.60N_{p\text{-}\mathrm{NO_2}}$	0.03	0.988	±0.15	35
2.	*m*-Chlorobenzyl	$0.21Y_{\mathrm{OTs}}$	$0.79N_{p\text{-}\mathrm{NO_2}}$	−0.04	0.977	±0.18	34
		$0.25Y_{\alpha\text{-}\mathrm{Bu}}$	$0.78N_{p\text{-}\mathrm{NO_2}}$	−0.08	0.986	±0.14	34
		$0.35Y_{\mathrm{neo}}$	$0.79N_{p\text{-}\mathrm{NO_2}}$	−0.02	0.989	±0.12	34
		$0.45Y_{\Delta}$	$0.81N_{p\text{-}\mathrm{NO_2}}$	−0.01	0.992	±0.11	34

a) $N_{p\text{-}\mathrm{NO_2}} = \log(k/k_{\mathrm{80E}})_{p\text{-Nitrobenzyl OTs}}$. b)c)d) See footnotes b, c, and d of Table 5.

$\log(k/k_{\mathrm{80E}})_1$ of **1** for Y_{Bz} and $\log(k/k_{\mathrm{80E}})_4$ for N_{Bz} results in such an excellent linearity as in Fig. 4, with a distinctly high precision of SD = ±0.065 and $R = 0.997$;

$$\log(k/k_{\mathrm{80E}})_3 = 0.48\log(k/k_{\mathrm{80E}})_1 + 0.51\log(k/k_{\mathrm{80E}})_4 - 0.024. \quad (9)$$

This may imply that there exists a unique common set of Y_{Bz} and N_{Bz} scales potentially applicable to solvolyses of substituted benzyl tosylates. Alternatively, this might be interpreted as a case of fortuitous conformity of the simple similarity correlation with two reference extremes, the $\log(k/k_{\mathrm{80E}})$ values for **1** and **4**. While the two reference benzyl substrates show high response to either the polarity or the nucleophilicity of solvent, neither Y nor N parameter may remain exactly the same between the two reference substrates. The precise conformity of this treatment may thus be largely because the solvation behavior (measured by N and Y scales) of **3** is intermediate between those of **1** and **4**.

It should be noted that the conventional N_{OTs} does not show an exact linearity with the nucleophilicity quantities derived from either **4** or **5**, over a wide range of solvent nucleophilicity. While general lN linearity has often been claimed, we have recently demonstrated that there is a clear trend of curvature in the plot of the nucleophilicity quantities against the standard N_{OTs} parameter for most of primary and secondary alkyl tosylates.[17)] The statistical m values evaluated by Eq. 6 for moderately deactivated benzyl derivatives cannot be free from the discrepancy due to the enforced linearity of the nucleophilicity term.

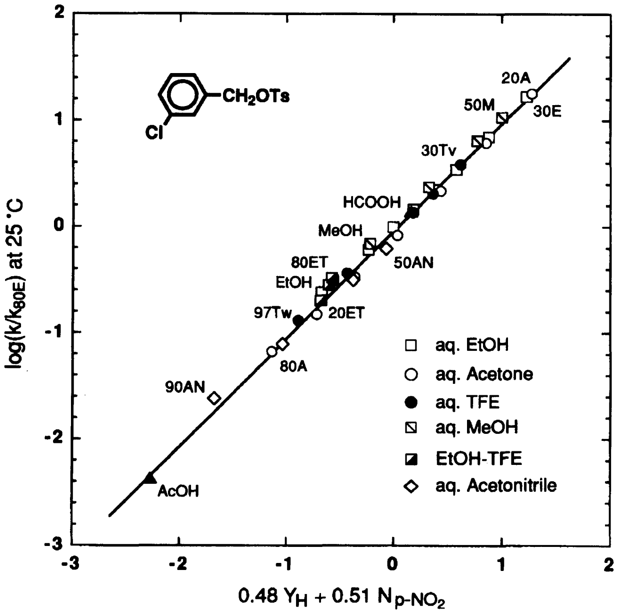


Fig. 4. Solvent effect on the solvolysis of *m*-chlorobenzyl tosylate; $Y_{\mathrm{H}} = \log(k/k_{\mathrm{80E}})_{\text{Benzyl OTs}}$ and $N_{p\text{-}\mathrm{NO_2}} = \log(k/k_{\mathrm{80E}})_{p\text{-Nitrobenzyl OTs}}$.

From the mechanistic point of view, the precise Winstein–Grunwald correlation by Eq. 1 as well as Eq. 6 can be interpreted on the basis of the assumption that a single reaction process of a common mechanism is operative in a wide range of solvents. The m value can be a measure of the degree of carbocation formation or the degree of bond-breaking of leaving tosylate group, and the l value can be a measure of the degree of bond-formation with a solvent nucleophile at the solvolysis transition state. Simultaneous mY and lN linearity relations should refer to the operation of a single-step concerted displacement mechanism which is extended to the $\mathrm{S_N2}$ (intermediate) mechanism.[4,15)] The m and l values change in a compensating way with substituents for a series of substituted benzyl derivatives, and the way of change is in line with the concept of a continuous spectrum of $\mathrm{S_N2}$–$\mathrm{S_N1}$ solvolysis mechanisms advocated by Schleyer and Bentley.[4)] Mechanistic change in the benzyl solvolysis occurs significantly with substituents over the range from the $\mathrm{S_N1}$ extreme for strongly electron-donating substituents, via a spectrum of $\mathrm{S_N2}$ mechanisms of varying looseness for moderately activating or weakly deactivating substituents, to the $\mathrm{S_N2}$ extreme for strongly deactivated **4** and **5**. The m and l values for strongly deactivated benzyl tosylates, **4** and **5**, indicate that the transition state for solvolysis of these substrates lies at nearly the same position on the reaction coordinate for the $\mathrm{S_N2}$ extreme in the continuous spectrum of $\mathrm{S_N1}$–$\mathrm{S_N2}$ mechanisms, and moves no more on further deactivation of the benzyl substrate by *p*-nitro and 3,5-bistrifluoromethyl substituents. The transition state is as tight as that for the $\mathrm{S_N2}$ solvolysis of ethyl and methyl tosylates.

Experimental

Materials: Benzyl tosylates were prepared by the Schotten–Bauman method,[14b] as described before;[14d] *p*-nitro derivative **4**, recrystallized from benzene, mp 102.7—103.4 °C, lit,[18] mp 105.0—105.5 °C. Anal. Found: C, 54.81; H, 4.32; N, 4.54%. Calcd for $C_{14}H_{13}NO_5S$: C, 54.72; H, 4.26; N, 4.56%.

3,5-Bistrifluoromethyl derivative **5**, mp 79.0—79.8 °C, recrystallized from ether–hexane. Anal. Found: C, 48.35; H, 3.12%. Calcd for $C_{16}H_{12}O_3SF_3$: C, 48.25; H, 3.04%. Ethyl and methyl tosylates commercially available were purified by recrystallization.

Organic solvents and water were purified as described before.[2,12] Binary solvents were prepared by mixing corresponding volumes or weights of pure solvents at 25 °C.

Kinetic Measurements: Solvolyses in aqueous binary solvents were followed conductimetrically using 10^{-4}—10^{-5} mol dm^{-3} solution of the starting tosylate in a thermostatted bath at an appropriate temperature controlled within ±0.01 °C as described before.[2] The rates of solvolysis for less reactive substrates at a higher temperature were followed by using the ampoule technique, with conductivity determination as described before.[2] The rates of all acetolyses and several slow solvolyses in the less aqueous organic solvents were determined by the ordinary titrimetric method using the usual ampoule technique.[19]

The experimental errors in conductivity runs were generally far less than 1.0%. The rate constants from titrimetric determination were slightly less accurate, but reproducible from run to run within an accuracy of 1.5%.

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