Solvent Effects on the Solvolysis of Neophyl Tosylates[1)]

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Solvolysis rates of 2-phenyl-2-methylpropyl and 2-(*p*-methoxyphenyl)-2-methylpropyl *p*-toluenesulfonates were determined in a wide variety of solvents and the solvent effects were analyzed based on the Winstein–Grunwald equation. The solvent effect on neophyl solvolyses failed to give a single linear correlation with the 2-adamantyl Y_{OTs} parameter. There was dispersion behavior for the respective binary solvent series between neophyl k_Δ substrates and 2-adamantyl tosylate. The pattern of dispersion could not be interpreted in terms of nucleophilic solvent assistance. The response to the solvent polarity (m value for each binary solvent series) was significantly lower for both the methoxy and the unsubstituted derivatives than the m=1.0 for the limiting k_c solvolysis, and appreciably lower for the methoxy derivative than for the unsubstituted one. Linearity of the solvent effects between both neophyl systems and also between other k_Δ substrates implied the existence of a unique kinetic solvent polarity scale Y_Δ characteristic of the β-aryl-assisted (k_Δ) solvolysis. The dispersion behavior and reduced m value for the k_Δ solvolysis were compatible with the entire π-delocalization of cationic charge between the assisting aryl-ring and the reaction center in the transition state.

The Winstein–Grunwald equation (1) has been widely used as a mechanistic probe for characterizing solvolytic processes, especially for detecting nucleophilic solvent-assistance,[1–5)]

$$\log(k/k_0) = mY + lN \qquad (1)$$

where k is the rate constant for solvolysis in any solvent and k_0 is the rate measured in 80% v/v aqueous ethanol; m is the sensitivity of the solvolysis to the solvent ionizing power, Y, and l is the sensitivity to the solvent nucleophilicity, N. Schleyer and Bentley recommended the preferred use of Y_{OTs} and N_{OTs} scales for the description of tosylate reactivities, based on 2-adamantyl and methyl tosylates as reference substrates, respectively.[5)] The Winstein–Grunwald relation has thus furnished the most practical, general application, and mechanistically significant approach.

2-Phenyl-2-methylpropyl *p*-toluenesulfonates (neophyl tosylates) are appropriate model substrates solvolyzing by the aryl assistance mechanism uncomplicated by either internal return or nucleophilic solvent assistance.[5–7)] From a mechanistic point of view, one may therefore expect that the neophyl solvolysis would be a simple linear function of solvent polarity and that the solvent effect can be correlated linearly in terms of the ionizing power scale Y_{OTs}, free of the involvement of the solvent nucleophilicity,

$$\log(k/k_0) = mY_{\mathrm{OTs}} \qquad (2)$$

Schleyer and others noted earlier that the solvolysis rates of 2-adamantyl tosylate correlated linearly with those for *p*-methoxyneophyl tosylate in various solvents where common data were available, and also with those for neophyl tosylate in typical solvolyzing solvents including ethanol and trifluoroacetic acid.[5)] Similarly, Roberts reported a linear relationship between the log k values for neophyl and 2-adamantyl tosylates for a range of varying aqueous ethanol mixtures and acetic acid-formic acid mixtures.[8)] On the other hand, Nair and Nair reported a Winstein–Grunwald correlation for the solvolysis of neophyl bromide with an m value of 0.94 and an l value of 1.15 in Eq. 1.[9)] This large l value may be indicative of an even greater response to the solvent nucleophilicity in the neophyl solvolysis than the response in the solvolysis of methyl tosylate. There are serious conflicts among these conclusions, even though they are all based on limited solvent sets. Our attention has thus been directed especially to the fact that the solvent effect on the neophyl solvolysis which should be mechanistically free of nucleophilic solvent assistance is not directly related with the Y_{OTs} parameter defined by the k_c solvolysis of 2-adamantyl tosylate, contrary to what has been pointed out in the literature.[10)] Winstein–Grunwald type treatment of the solvent effects on the solvolysis rate for *p*-methoxyneophyl tosylate appears to require definition of an alternative scale of solvent polarities, characteristic of k_Δ solvolyses. Furthermore, it would be of particular interest to utilize the deviation from the linearity against Y_{OTs} (i.e., from Eq. 2) as a probe for estimating the degree of aryl participation, in an analogous manner to Eq. 1 for detecting the involvement of the nucleophilicity.[11)] However, the data in the literature[6)] concerning the aryl-assisted k_Δ solvolysis in varying solvents are not sufficient for our purpose of close comparison with the Schleyer–Bentley Y_{OTs} scale.[5)] Accordingly, we have determined the solvolysis rates of neophyl and *p*-methoxyneophyl tosylates in a wide variety of solvents, to make it possible to compare with the solvent effect on nucleophilically limiting k_c solvolyses.

The present paper is mainly concerned with the behavior of *p*-methoxyneophyl and unsubstituted neophyl tosylates in the kinetic solvent effect and the derivation of an ionizing power scale most suitable to aryl-assisted solvolysis.

Results

Solvolysis rates of neophyl and *p*-methoxyneophyl tosylates were determined in a wide variety of solvents. The rate measurement in aqueous organic solvents was carried out mostly by the conductometric method, and the measurement in organic acids was made by the ordinary titrimetric method. The solvolysis of neophyl tosylate is inconveniently slow in most aqueous solutions to follow directly at 25 °C; therefore, we have determined the relative rates at 45 °C at which rates were measured directly covering a wider range of solvents for both neophyl and *p*-methoxyneophyl tosylates. The results are summarized in Tables 1 and 2, together with relevant literature data, and also included are the $\log(k/k_{80E})$ values of solvolyses of 2-adamantyl tosylate at 45 °C,[10] which were used in the following correlation analysis instead of the ordinary Y_{OTs} values.

In Fig. 1, solvolysis rates of neophyl and *p*-methoxyneophyl tosylates are plotted, on a logarithmic scale, against the corresponding rates of 2-adamantyl tosylate. The 2-adamantyl Y_{OTs} parameter apparently gave no simple linear relationship for either neophyl or *p*-methoxyneophyl tosylate. Aqueous ethanol and aqueous acetone plots fell on separate lines with different slopes, and the plots for less nucleophilic solvents, acids and fluorinated alcohols, lay above the aq acetone line. The pattern of deviations was clearly inconsistent with that expected for mechanistic involvement of the solvent nucleophilicity. The pattern appeared to be quite similar for both neophyl substrates, but slightly more extensive for the *p*-methoxy derivative.

These present results were not in line with the previous conclusions concerning this solvolysis reported by Schleyer et al.[5] and by Roberts.[8] Linear correlation with the adamantyl Y_{OTs} scale could be obtained only for each binary solvent series, as listed in Table 3. Correlations (Entries 5,6,11, and 12) for a limited solvent series excluding either aq ethanol (aq methanol) mixtures or aq acetone mixtures did not show any significant improvement in the linearity for both substrates. This fact argued against Roberts' conclusion[8] of a simple linear correlation with the 2-adamantyl Y_{OTs} scale (Eq. 2) for neophyl tosylate solvolysis.

In Fig. 2, the logarithmic rates of solvolyses of *p*-methoxyneophyl tosylate are plotted against those for neophyl tosylate, giving a slope appreciably lower than unity

$$\log k_{p\text{-MeO}} = 0.803 \log k_{\mathrm{H}} + 0.830$$

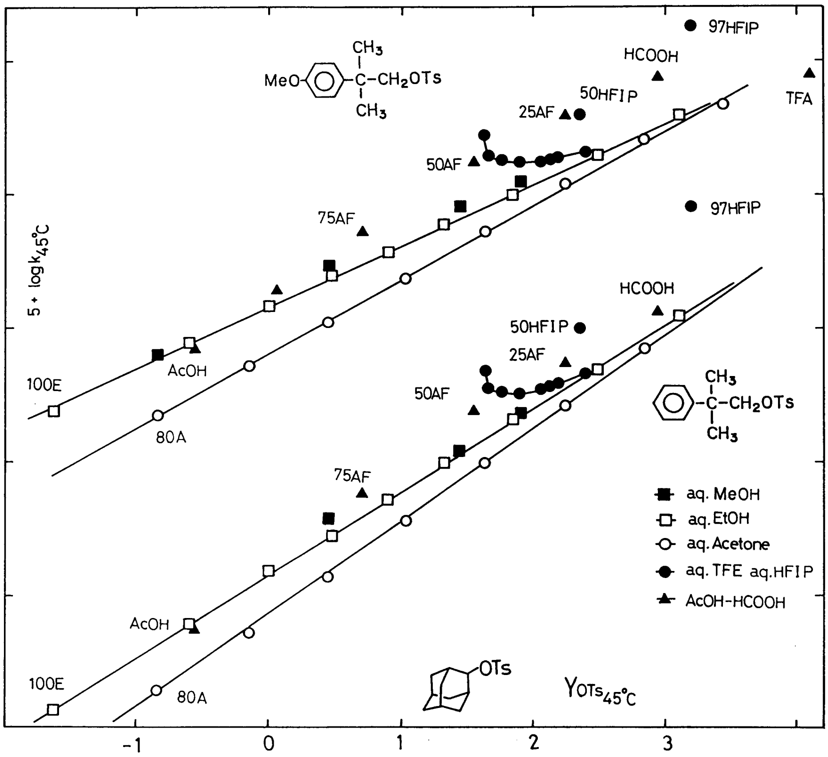

Fig. 1. The mY plots of unsubstituted (lower trace) and *p*-MeO (upper trace) neophyl tosylates; abscissa is the $\log(k/k_{80E})$ value of 2-adamantyl tosylate at 45 °C.

Table 1. Solvolysis Rates of Neophyl Tosylates

Solvent[a]	Neophyl OTs		*p*-Methoxyneophyl OTs	
	Temp/°C	$10^5 k/s^{-1}$	Temp/°C	$10^5 k/s^{-1}$
EtOH	25	0.00076[b]	25	0.207, 0.179[c]
	45	0.0133[b]	45	2.41, 2.34[b]
	50	0.02564[c]	50	4.23[c]
	75	0.523[d]		
90E	25	0.00420[e]	25	0.712
	45	0.0608,[e] 0.0564[b]	45	7.78
	50	0.105[f]		
	60	0.3655		
	75	1.80[f]		
	85	5.204		
80E	25	0.0108[e]	25	1.406[c]
	45	0.151,[e] 0.143[b]	45	14.85, 15.14[b]
	50	0.27[c]	50	26.2[c]
	60	0.8895		
	70	2.86[f]		
	75	4.486		
70E	45	0.2839, 0.323[b]	25	2.343
	50	0.578[f]	45	24.83
	75	8.2[f]		
60E	25	0.0420,[e] 0.032[g]	25	3.60, 3.75[c]
	45	0.520, 0.514[g]	45	36.8
	75	13.16	55	103
50E	25	0.0825,[e] 0.0583[g]	25	5.995
	45	0.988, 0.89[h]	45	60.7
	75	24.0		
40E	25	0.192[g]	25	11.41
	45	2.07, 3.3[g]	45	101
30E	25	0.511	25	25.73
	45	4.92	45	194.6
20E	45	12.4	45	389
80A	25	0.00123[e]	25	0.174
	45	0.0195[e]	45	2.23
	75	0.678	75	53.0[c]
	115	32.8		
70A	45	0.0529[e]	25	0.453
	55	0.187	45	5.22
	75	1.87	75	134
60A	45	0.138	25	1.062
			45	11.27
50A	45	0.363	25	2.372
			45	23.5
40A	45	0.9806	25	5.90
			45	52.2
30A	45	2.621	25	14.54
			45	120.4
20A	25	0.700	0	1.453
	45	7.04	25	32.1
			45	256
10A			25	41.1
			45	467
MeOH			25	0.510[c]
			45	6.37[b]
			50	11.4[c]

a) Volume percent (v/v) of organic component except where stated otherwise. Abbreviations; E=EtOH, M=MeOH, A=acetone, T=TFE=2,2,2-trifluoroethanol, HFIP=1,1,1,3,3,3-hexafluoro-2-propanol, AF=acetic acid–formic acid (volume%, AcOH). Suffix w means weight% (w/w) of organic component. b) Values were calculated from data in the literature at other temperatures. c) Ref. 6. d) A. Diaz, I. Lazdins, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 6546 (1968). e) Values were calculated from data at other temperatures. f) D. D. Roberts and R. C. Snyder, Jr., *J. Org. Chem.*, **45**, 4052 (1980). g) Ref. 8. h) D. D. Roberts, *J. Org. Chem.*, **47**, 561 (1982). i) Ref. 20. j) Ref. 19. k) S. Winstein and R. Heck, *J. Am. Chem. Soc.*, **78**, 4801 (1956). l) M. G. Jones and J. L. Coke, *ibid.*, **91**, 4284 (1969). m) T. Ando, S.-G. Kim, K. Matsuda, H. Yamataka, Y. Yukawa, A. Fry, D. E. Lewis, L. B. Sims, and J. C. Wilson, *ibid.*, **103**, 3505 (1981). n) Buffered with NaOCHO.

Table 1. (Continued)

Solvent[a]	Neophyl OTs		*p*-Methoxyneophyl OTs	
	Temp/°C	$10^5\,k/\mathrm{s}^{-1}$	Temp/°C	$10^5\,k/\mathrm{s}^{-1}$
80M	45	0.374	25	2.87[c]
			45	29.5[b]
			50	50.5[c]
60M	45	1.21	25	9.97
			45	80.7, 85.6[e]
			50	143[c]
50M	45	2.37	25	15.2
			45	125.8
TFE	45	4.82	25	32.0
			45	281
97Tw	45	3.57	25	23.15
			45	197.1
80T	45	3.316	25	19.90
			45	183.6
70Tw	45	3.270	25	19.0
			45	173.6
50T	45	3.562	25	18.44
			45	178.9
50Tw	45	3.678	45	180.6
40T	45	3.884	25	19.21
			45	191.7
30T	45	4.714	25	21.61
			45	210.7
97HFIPw	25	11.2	0	15.1
	45	81.1	25	258
			45	1819[e]
50HFIP	45	9.89	25	50.4
			45	394
TFA	0	4.97[d]		
	25	100[d]		
	45	786[b]		
AcOH	25	0.00330,[b] 0.00309[b]	25	0.571,[e] 0.537[i]
	45	0.05446[b]	25.06	0.532[k]
	50	0.101,[i] 0.0987[l]	35	2.10[m]
	74.71	1.93[j]	40	3.838
	75	2.00,[i] 1.92[l]	45	6.73,[b] 7.03,[e] 6.66[b]
	99.58	24.7[j]	50	12.1,[k] 12.8,[l] 11.8,[m] 11.9[i]
			55	22.39
			65	63.5
90AF			45	18.9
75AF	30	0.075[g]	25	5.5[c]
	45	0.58[g]	45	52.8
65AF	25	0.0833[g]		
	45	1.06[g]		
50AF	25	0.134[g]	25	17.2[c]
	45	2.2,[g] 2.385	45	175.6
25AF	30	0.89[g]	25	42.54
	45	5.5[g]	45	393
HCOOH	25	1.16[d]	0	3.22
	45	13.14[b]	15	24.3
	50	23[d]	25	81.4, 83.1[k,n]
			45	754[e]

with a precision of SD=±0.08 and a correlation coefficient of 0.994 for all solvents. This correlation may well be regarded as a single linear relationship without statistically significant dispersion, in reference to an ordinary precision criterion, an SD of ca. ±0.15, for general conformity of the Bentley–Schleyer analysis.[5] While the points for aq ethanol, aq acetone, and acid mixtures fell on less significantly separate lines, there was no significant difference in the solvent behavior of both neophyl substrates, both with a reduced response to the solvent polarity; the specific solvation of the methoxy substituent itself did not appear to be important in the neophyl solvolysis.

While direct *mY* treatment of Eq. 2 with the 2-

Table 2. Solvolysis of Neophyl Tosylates at 45 °C and Solvent Parameters

Solvent[a)]	Neophyl OTs			*p*-MeO-Neophyl OTs			Y_{OTs}[c)] (45 °C)	N_{OTs}[d)]
	$10^5 k/s^{-1}$	$\Delta H^{\ne}$[b)] kcal mol^{-1}	$\Delta S^{\ne}$[b)] e.u.	$10^5 k/s^{-1}$	$\Delta H^{\ne}$[b)] kcal mol^{-1}	$\Delta S^{\ne}$[b)] e.u.		
EtOH	0.0133	26.3	−7.4	2.41	22.5	−9.1	−1.63	0.00
90E	0.0608	24.6	−9.9	7.78	21.9	−8.6	−0.60	0.01
80E	0.151	24.2	−9.1	14.85	21.7	−7.9	0.00	0.00
70E	0.284	23.1	−11.2	24.83	21.6	−7.2	0.46	−0.05
60E	0.520	23.1	−10.3	36.8	21.1	−7.9	0.89	−0.09
50E	0.988	22.8	−10.0	60.7	21.2	−6.8	1.32	−0.11
40E	2.07	21.8	−11.7	101	19.9	−9.8	1.84	−0.22
30E	4.92	20.7	−13.3	194.6	18.4	−13.1	2.48	−0.31
20E	12.4			389			3.1	−0.34
MeOH				6.37	23.2	−5.1	−0.85	−0.04
80M	0.374			29.5	21.3	−7.8	0.45	−0.05
60M	1.21			80.7	19.1	−12.9	1.44	−0.13
50M	2.37			125.8	19.3	−11.3	1.90	−0.19
80A	0.0195	25.4	−9.5	2.23	23.4	−6.4	−0.84	−0.42
70A	0.0529	25.5	−7.2	5.22	22.9	−6.4	−0.15	−0.38
60A	0.138			11.27	21.6	−8.7	0.44	−0.34
50A	0.363			23.5	21.0	−9.3	1.03	−0.35
40A	0.9806			52.2	19.9	−11.1	1.63	−0.39
30A	2.621			120.4	19.3	−11.4	2.24	−0.40
20A	7.04	21.1	−11.3	256	18.9	−11.1	2.84	−0.44
10A				467	22.2	0.7	3.44	−0.41
TFE	4.82			281	19.8	−8.0	1.64	−3.0
97Tw	3.57			197.1	19.6	−9.6	1.66	−2.79
80T	3.316			183.6	20.3	−7.3	1.76	−1.90
70Tw	3.270			173.6	20.2	−7.7	1.89	−1.20
50T	3.562			178.9	20.8	−5.9	2.05	−1.14
50Tw	3.678			180.6			2.12	−0.95
40T	3.884			191.7	21.1	−4.9	2.18	−0.92
30T	4.714			210.7	20.8	−5.4	2.39	−0.80
97HFIPw	81.1	18.0	−16.1	1819	17.8	−10.8	3.19	−4.27
50HFIP	9.89			394	18.7	−10.7	2.35	−1.78
TFA	786	18.8	−9.2				4.1	−5.56
AcOH	0.05446	25.8	−6.3	7.03	23.0	−5.3	−0.56	−2.35
90AF				18.9			0.06	−2.35
75AF	0.58	25.5	−2.5	52.8	20.7	−8.6	0.70	−2.35
65AF	1.06	23.3	−8.1					
50AF	2.385	25.7	0.9	175.6	21.3	−4.4	1.55	−2.35
25AF	5.5	22.6	−7.0	393	20.3	−5.8	2.24	−2.35
HCOOH	13.14	22.2	−6.5	754	20.3	−4.6	2.94	−2.35

a) See footnote a in Table 1. b) 1 cal=4.184 J and 1 e.u.=4.184 J K^{-1} mol^{-1}. c) Log (k/k_{80E}) for 2-adamantyl tosylate at 45 °C; data taken from Ref. 10. d) Refs. 5, 10, and T. W. Bentley and G. E. Carter, *J. Org. Chem.*, **48**, 579 (1983).

adamantyl Y_{OTs} parameter did not give a satisfactory correlation for all solvents, as shown in Table 3, Eq. 1 involving the lN term gave an appreciably improved correlation with a negative contribution of solvent nucleophilicity. The results of correlation analysis based on Eq. 1 are summarized in Table 4. Essentially the same correlation with a negative l value was provided for a partial solvent set excluding the aqueous acetone series (Entries 4 and 8) with excellent precision. The same was true for a partial correlation (Entries 3 and 7) excluding the aqueous alcoholic series, giving an improved correlation with a definitely negative l value of −0.2. On the other hand, the sets (Entries 2 and 6) consisting of only the aq acetone and aq ethanol series resulted in excellent correlations with high l values of l=0.85 for the unsubstituted derivative and l=0.94 for the *p*-MeO derivative, leading to a clearly unreasonable interpretation of the neophyl solvolysis in terms of the k_s bimolecular nucleophilic displacement mechanism. This may be compared to the analysis result reported by Nair and Nair for the solvolysis of neophyl bromide.[9)]

The solvent effect on the neophyl solvolysis was characterized by a dispersion pattern of each binary solvent series with significantly reduced m values (0.5—0.8). Dispersion between various binary solvent mixtures in Fig. 1 should be due not to solvent nucleophilicity, but to certain other factors associated with the aryl-assisted ionization process.

Table 3. Results of Correlations by Eq. 2

Tosylate No.	(Solvent)	$mY_{\mathrm{OTs}}+c$ m	c	R[a]	SD[b]	n[c]
Neophyl						
1	All	0.75±0.03	−0.12	0.968	±0.25	35
2	EW[d]	0.62±0.003	−0.02	0.9999	±0.01	9
3	AW[e]	0.70±0.01	−0.33	0.9998	±0.02	7
4	AF[f]	0.68±0.04	0.03	0.995	±0.11	5
5	Exc. EW,MW[g]	0.83±0.05	−0.25	0.966	±0.27	23
6	Exc. AW[h]	0.74±0.04	−0.03	0.971	±0.23	28
p-Methoxyneophyl						
7	All	0.54±0.03	−0.04	0.955	±0.22	37
8	EW[d]	0.46±0.004	−0.01	0.9997	±0.02	9
9	AW[e]	0.55±0.01	−0.36	0.9996	±0.03	8
10	AF[f]	0.59±0.03	0.08	0.995	±0.08	6
11	Exc. EW,MW[g]	0.59±0.05	−0.12	0.941	±0.25	24
12	Exc. AW[h]	0.53±0.02	0.05	0.972	±0.16	29

a) Correlation coefficients. b) Standard deviations. c) Numbers of data points involved. d) Partial correlation of aqueous ethanol series. e) Partial correlation of aqueous acetone series. f) Partial correlation of acetic acid–formic acid mixtures. g) Excluding aqueous ethanol and aqueous methanol series. h) Excluding aqueous acetone series.

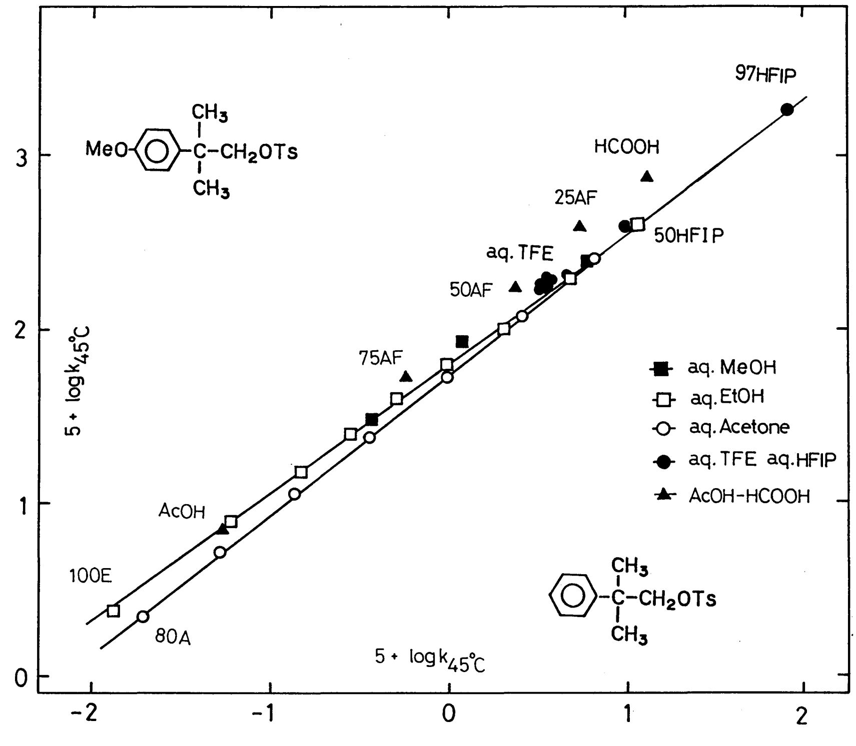

Fig. 2. Logarithmic rate plots of solvolysis of *p*-MeO vs. unsubstituted neophyl tosylates.

Discussion

The important features of the present results are summarized as follows.

i) The response (m value) to the solvent polarity Y_{OTs} in any solvent series was significantly lower for both methoxy and unsubstituted neophyl tosylates than the m value of unity for limiting k_c solvolysis of 2-adamantyl tosylate, and was relatively lower for the methoxy derivative than for the unsubstituted tosylate.

ii) The 2-adamantyl Y_{OTs} parameter failed to give a single straight line correlation for the solvent effect on the

Table 4. Results of Correlations by Eq. 1

Tosylate No. (Solvent)	$mY_{\mathrm{OTs}}+lN_{\mathrm{OTs}}+c$ m	l	c	R[a)]	SD[b)]	n[c)]
Neophyl						
1 All	0.67±0.02	−0.17±0.02	−0.19	0.988	±0.15	35
2 EW,AW[d)]	0.70±0.01	0.85±0.07	0.01	0.999	±0.04	16
3 Exc. EW,MW[e)]	0.72±0.02	−0.20±0.02	−0.41	0.996	±0.10	23
4 Exc. AW[f)]	0.66±0.02	−0.15±0.02	−0.10	0.991	±0.13	28
p-Methoxyneophyl						
5 All	0.50±0.02	−0.15±0.02	−0.14	0.979	±0.15	37
6 EW,AW[d)]	0.55±0.01	0.94±0.07	0.02	0.999	±0.04	17
7 Exc. EW,MW[e)]	0.57±0.02	−0.21±0.02	−0.40	0.992	±0.10	24
8 Exc. AW[f)]	0.49±0.02	−0.12±0.02	−0.04	0.991	±0.09	29

a), b), c) See footnotes a, b, and c in Table 3. d) Partial correlation of aqueous ethanol and aqueous acetone series. e) See footnote g in Table 3. f) See footnote h in Table 3.

neophyl solvolysis. The deviation from simple linearity could not be rationalized in terms of a mechanistic involvement of the solvent nucleophilicity.

iii) There was dispersion behavior for the respective binary solvent series' in the dependence upon the polarity (Y) scale between the present neophyl substrates and 2-adamantyl tosylate.

The treatment with Eq. 1 resulted in a negative lN contribution with $l\cong-0.2$ for the neophyl solvolysis (Table 4). Whereas the size of the l value was not very large, the relative importance, l/m value, was statistically rather significant. If this lN term in the neophyl correlation was ascribed to the nucleophilicity, such a negative l value would lead to a conclusion of significant involvement of the solvent nucleophilicity in the solvolysis of 2-adamantyl tosylate. The negative lN term should produce even enhanced divergence between aq ethanol and aq acetone lines for both neophyl substrates. It was evident that the pattern of dispersion could never be explained by simply invoking the nucleophilic solvent assistance.

It was quite serious that the neophyl solvolysis showed no linear response to the solvent polarity as expected for its nucleophilically limiting mechanism. Essentially the same dispersion pattern has been observed in the plots against the 2-adamantyl Y_{OTs} for similar aryl-assisted solvolyses of *trans*-2-(*p*-methoxyphenyl) cyclopentyl, 2,2-bis(*p*-methoxyphenyl)ethyl, *threo*-2-(*p*-methoxyphenyl)-1-methylpropyl, and 2-(*p*-methoxyphenyl)-1-methylethyl tosylates,[11)] none of which involved significant solvent nucleophilic assistance. More significant, single straight line correlations have been obtained for all these solvolyses against the logarithms of solvolysis rates of *p*-MeO-neophyl tosylate. The direct logarithmic rates correlation between *p*-MeO-neophyl tosylate and the unsubstituted neophyl tosylate in Fig. 2 afforded a linear plot with little dispersion; practically, deviations within at most 0.2 are too small to warrant interpretation. There should be unique dispersion behavior characteristic of aryl-assisted solvolysis, and a common Y scale correlating the solvent effects on aryl-assisted solvolyses. On the other hand, the solvolysis of *exo*-norbornyl tosylate, a typical example of the σ-participation process, showed no significant dispersion of aq ethanol and aq acetone lines in the plot against the 2-adamantyl-based Y_{OTs}.[10)] Similarly, 1,2,2-trimethylpropyl tosylate also did not show significant dispersion behavior at all.[10,12)] The solvent effects of these substrates were all closely, though not perfectly, related with the 2-adamantyl Y_{OTs}, commonly showing a slight downward separation of aq fluorinated alcohols and acetic–formic acids.[10,12)] The dispersion pattern of the plot against the 2-adamantyl Y_{OTs} should have been characterstic of the aryl-assisted process, but a quantitative explanation was difficult to formulate. Similarly, the dispersion behavior has been noted in the analysis of solvent effects on the solvolysis of benzhydryl chloride,[2a,e,13)] 1-phenylethyl chlorides,[2a,c,14)] and the related halides[2d,e,15,16)] and tosylates,[1,10,17)] leading to a pessimistic view that it is probably not feasible to devise a generally applicable kinetic solvent scale for S_N1 reactions.[13)]

It has recently been suggested that a wide range of dispersion behavior can be argued most reasonably by differences in solvation between aromatic ring and alkyl groups.[1,2a,d,10,13,15,16)] The effect may be due to charge-delocalization between the aryl-ring and the carbenium center in the transition state. The dispersion behavior of neophyl substrates appears to be caused by aryl-bridging in the transition state.[1,10)] Aryl-bridging and σ-assisted transition states should differ significantly in the effectiveness of the charge delocalization.

In the aryl-assisting mechanism, the neighboring aryl group plays the role of an intramolecular nucleophile displacing the leaving group. The developing charge at the reaction center in the transition state of this process is entirely delocalized through effective π-overlapping with the participating aryl group. This may cause a significant loss of the highly oriented specific solvation at the reaction center, lowering the m value from unity. The charge-delocalization enhanced by the *p*-methoxy substituent makes the dispersion of the mY_{OTs} plot more significant accompanied by a lower response to the solvent polarity than that of the unsubstituted derivative.

Roberts pointed out that there is a characteristically different response to solvent effect by a substrate ionizing with neighboring-group assistance by bridging from one ionizing with assistance by exalted hyperconjugation.[8] Each binary solvent series shows different responses depending upon localized charge at the reaction center in the transition state. While the simple pattern recognition method reported by Roberts may well serve as a useful test for differentiating mechanisms, his particular choice of solvent systems, aq ethanol and acetic–formic acid mixtures, does not appear to be generally appropriate. Roberts was, in fact, unable to differentiate between the dispersion behavior of the neophyl k_Δ mechanism and the 2-adamantyl k_c mechanism. It should be particularly noted that inclusion of the aq acetone series enables us to differentiate between aryl- and σ-bridging solvolyses as well as between aryl-assisted and limiting k_c solvolyses.

The dispersion behavior in the k_Δ solvolyses of β-arylalkyl derivatives can be recognized more distinctly by introducing a binary aqueous acetone solvent series into the correlation. In the aqueous acetone series, the ionizing power is increased significantly in parallel with the water content while the solvent nucleophilicity N is kept relatively constant at -0.4 over a range of Y values. Because of a small difference in nucleophilicity ($\Delta N<0.4$) between the aqueous ethanol and aqueous acetone series, any solvolyses belonging to the S_N1 mechanism category (displacement with a loose transition state rather than a tight one) should never show such a significant dispersion (no more than 0.2 in log k) between both binary solvent series arising from nucleophilic solvent assistance. Nevertheless, the mY plot often displays a significant gap between both solvent series, which might be referred to as a remarkable, but clearly unreasonable, contribution of solvent nucleophilicity; for this reason, the previous conclusion of significant involvement of the nucleophilicity in the neophyl solvolysis may be invalidated.

There seems to be a unique set of Y_Δ values applicable to aryl-assisted solvolysis. The polarity scale based on the neophyl solvolysis appears to have particular applicability not only to aryl-assisted solvolyses but also, at least qualitatively, to the solvolyses of benzylic tosylates.[11,17] Winstein pointed out that neophyl chloride was more suitable for correlation of the rates of solvolysis of the 1-phenylethyl and benzhydryl chlorides than is the *t*-butyl chloride on which the Winstein Y parameters are based.[2a,d] This is not surprising because both the aryl-assisted and the benzylic solvolyses should involve a significant π-delocalization interaction with the incipient carbocation charge. Further application of the Y_Δ scale to the analysis of solvent effects will be reported in forthcoming papers.

Experimental

Materials: Neophyl and *p*-methoxyneophyl tosylates were prepared by the Tipson procedure[18] from the corresponding alcohol and *p*-toluenesulfonyl chloride in pyridine; recrystallized from ether–hexane; unsubstituted derivative, mp 74.5—75 °C (lit,[19] mp 74—75 °C); Found: C, 67.02; H, 6.60%. Calcd for $C_{17}H_{20}O_3S$: C, 67.08; H, 6.62%. *p*-MeO derivative, mp 46.5—47 °C (lit,[6] mp 44—46 °C); Found: C, 64.71; H, 6.65%. Calcd for $C_{18}H_{22}O_4S$: C, 64.65; H, 6.63%.

Anhydrous acetic acid, acetone, ethanol, and water were purified as described previously.[10,14,21] 2,2,2-Trifluoroethanol was refluxed for 2 h over anhydrous $CaSO_4$ and K_2CO_3,[22] fractionated, dried over Molecular Sieve 4A, and redistilled through a Widmer column. The middle fraction, bp 73—74 °C was used for preparation of the reaction solvent. 1,1,1,3,3,3-hexafluoro-2-propanol (purity>99.99%) obtained from Central Glass Co., Ltd., was used without further purification. Methanol was twice refluxed with sodium metal and the middle fraction was redistilled through a Widmer column.

Binary solvents were prepared by mixing corresponding volumes or weights of pure solvents at 25 °C.

Kinetic Measurement: Solvolyses in aqueous binary solvents were followed conductometrically.[10,14] Conductance measurements were made in a cell with bright platinum electrodes using approximately 25 or 50 cm^3 of 10^{-3}—10^{-4} mol dm^{-3} solution of the starting tosylate in a thermostated bath at an appropriate temperature controlled to within ±0.01 °C. For the conductivity measurements in aqueous solvents with a high water content, complete dissolution could be attained relatively quickly by first dissolving the substrate in a small amount of the organic solvent, and by adding this solution to the respective aqueous organic solvents added with an adjustable amount of water. Conductance readings were taken by using a conductivity meter (CM-50AT and CM-60S equipped with an interval time unit and printer, Toa Electronics Ltd.). Solvolyses were followed by taking at least 100 readings at appropriate intervals for 3 half-lives, and the infinity reading was taken after 10 half-lives. The conductance readings were then fitted to the first-order rate equation by means of a least-squares computer program; the precision of fit to first-order kinetics was generally satisfactory over 3 half-lives ($R>$ 0.99998).

The rates of acetolysis and formolysis were determined by the ordinary titrimetric method using the usual ampoule technique for less reactive runs at high temperatures and using the batch technique for relatively reactive runs.[21]

The experimental errors in respective runs were generally less than 1.0% and rate constants from repeated runs were reproducible within an accuracy of 1.5%.

References

1) Preliminary report, M. Fujio, M. Goto, K. Funatsu, T. Yoshino, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **17(2)**, 255 (1990).

2) a) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948). b) S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73**, 2700 (1951); A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770 (1956). c) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1579, 1602 (1957). d) A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1608

(1957). e) S. Winstein, A. H. Fainberg, and E. Grunwald, *ibid.*, **79**, 4146 (1957).

3) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York (1962).

4) T. W. Bentley and P. v. R. Schleyer, *Adv. Phys. Org. Chem.*, **14**, 1 (1977); T. W. Bentley and G. Llewellyn, *Progr. Phys. Org. Chem.*, **17**, 121 (1990).

5) F. L. Schadt, T. W. Bentley, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **98**, 7667 (1976).

6) S. G. Smith, A. H. Fainberg, and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

7) M. Fujio, K. Funatsu, M. Goto, M. Mishima, and Y. Tsuno, *Tetrahedron*, **43**, 307 (1987); M. Fujio, M. Goto, M. Mishima, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **63**, 1121 (1990); No ^{18}O-equilibration of the reactant sulfonate oxygens was observed in the acetolysis of neophyl tosylate (M. Fujio, F. Sanematsu, Y. Tsuno, M. Sawada, and Y. Takai, *Tetrahedron Lett.*, **29**, 93 (1988); *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **16(2)**, 193 (1988); *Nippon Kagaku Kaishi*, **1989**, 1371).

8) D. D. Roberts, *J. Org. Chem.*, **49**, 2521 (1984).

9) M. R. Nair and S. V. Nair, *Indian J. Chem., Sect. A*, **16**, 984 (1978).

10) M. Fujio, M. Goto, T. Yoshino, K. Funatsu, Y. Tsuji, S. Ouchi, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **16(1)**, 85 (1987).

11) Unpublished data.

12) Y. Tsuji, M. Fujio, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **17(2)**, 281 (1990).

13) C. A. Bunton, M. M. Mhala, and J. R. Moffatt, *J. Org. Chem.*, **49**, 3639 (1984).

14) S. Usui, Y. Shibuya, T. Adachi, M. Fujio, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **14(2)**, 355 (1984).

15) T. W. Bentley, I. S. Koo, and S. J. Norman, *J. Org. Chem.*, **56**, 1604 (1991).

16) K.-T. Liu, H.-C. Sheu, H.-I. Chen, P.-F. Chiu, and C.-R. Hu, *Tetrahedron Lett.*, **31**, 3611 (1990); K.-T. Liu and H.-C. Sheu, *J. Org. Chem.*, **56**, 3021 (1991).

17) M. Fujio, M. Goto, Y. Tsuno, S. Kobayashi, and H. Taniguchi, *Tetrahedron Lett.*, **31**, 7039 (1990).

18) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

19) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952).

20) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2763 (1956).

21) K. Funatsu, M. Fujio, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **13(1)**, 125 (1981); **13(2)**, 391 (1982).

22) Z. Rappoport and J. Kaspi, *J. Am. Chem. Soc.*, **96**, 4518 (1974).