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Solvent Effects on Anchimerically Assisted Solvolyses. II.[1) Solvent Effects in Solvolyses of *threo*-2-Aryl-1-methylpropyl *p*-Toluenesulfonates

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The solvent effects on the solvolysis of *threo*-2-aryl-1-methylpropyl *p*-toluenesulfonates were analyzed with the aid of the extended Winstein–Grunwald Equation. The aryl-assisted k_Δ solvolysis of 2-(*p*-methoxyphenyl)-1-methylpropyl and 2-methyl-2-phenylpropyl *p*-toluenesulfonates failed to give a single linear correlation with the Y_{OTs} parameter. The dispersion against Y_{OTs} cannot be due to nucleophilic solvent assistance. The m values from the plots of 2-(*p*-methoxyphenyl)-1-methylpropyl and 2-methyl-2-phenylpropyl *p*-toluenesulfonates against Y_{OTs} were significantly lower than m=1.0 for the limiting k_c solvolysis. Significantly improved correlations (R>0.99; SD<0.14) were obtained for the *p*-methoxy, 3-chloro-4-methoxy, and *p*-methyl derivatives with the Y_Δ scale based on the solvolysis of 2-(*p*-methoxyphenyl)-2-methylpropyl *p*-toluenesulfonate, instead of with Y_{OTs}. No improvement by the Y_Δ treatment was obtained for the unsubstituted compound (R=0.97; SD=0.22). A new similarity comparison analysis in terms of Y_{OTs} and Y_Δ, i.e., $\log(k/k_{80\mathrm{E}})=m_\mathrm{c}Y_{\mathrm{OTs}}+m_\Delta Y_\Delta$, was applied successfully to the present k_Δ solvolyses. The degree of Y_Δ character relative to the Y_{OTs} one, scaled by $m_\Delta/(m_\mathrm{c}+m_\Delta)$, varies for 1-methyl-2-phenylpropyl tosylates in the range from 1.0 to 0.00 in the consistent manner expected if the dispersion in the Y_{OTs} plot becomes less pronounced for solvolyses of less significant anchimeric assistance. There is a continuous spectrum of behavior between the extreme pure k_c mechanism and the extreme pure k_Δ one.

We have been conducting extensive investigations of the mechanisms of aryl-assisted solvolyses of 2-methyl-2-phenylpropyl *p*-toluenesulfonates (abbrev. to neophyl tosylates, hereafter) (**1**),[2) and related systems,[3,4) using substituent effect analysis, especially the Yukawa–Tsuno Equation (Eq. 1):[5)

$$\log(k/k_\mathrm{o})=\rho(\sigma^\circ+r\Delta\bar{\sigma}^+_\mathrm{R}). \tag{1}$$

Neighboring aryl-assisted processes generally gave good linear correlations with r values of 0.5—0.6.[2—4) The extensive resonance contribution indicated by these exalted r values provides strong evidence for enhanced π-delocalization through bridging in the rate-determining transition state between the β-aryl π-system and the carbenium center. Recently, we have extended our studies[2,3) to substituent effects in the solvolysis of *threo*-2-aryl-1-methylpropyl *p*-bromobenzenesulfonates (**2**-OBs).[4)

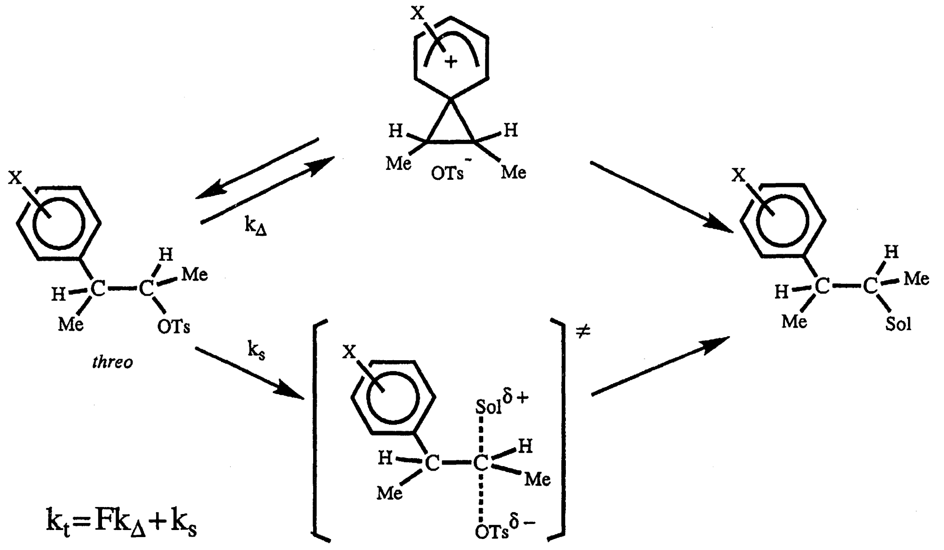
The Yukawa–Tsuno treatment has revealed that the solvolysis of **2** proceeds through two competing pathways, the aryl-assisted k_Δ pathway and the aryl-unassisted k_s one, shown in Scheme 1.[4,6) The ordinary β-aryl-assisted mechanism with a characteristic intermediate r value occurs only for substrates carrying strongly electron-donating substituents, and it shifts gradually to the aryl-unassisted mechanism having lower ρ- and r-values, for substrates carrying electron-attracting groups. Such a difference in mechanism should also be reflected by different solvents effects. Consequently, we are interested in the solvent effect for these and related β-arylalkyl compounds.

The dual-parameter Winstein–Grunwald Equation 2 has been widely employed as a mechanistic probe for characterizing solvolytic processes,[1,7—10)

$$\log(k/k_{80\mathrm{E}})=mY_{\mathrm{OTs}}+lN_{\mathrm{OTs}}. \tag{2}$$

In Eq. 2, k is the rate constant for solvolysis of a *p*-toluenesulfonate (tosylate) in any solvent, $k_{80\mathrm{E}}$ is the rate constant measured in 80% v/v aqueous ethanol, m is the sensitivity of the solvolysis rate to the solvent ionizing power Y_{OTs}, and l is the sensitivity to the solvent nucleophilicity, N_{OTs}.

For the solvolysis of neophyl tosylate (**1H**) which reacts by an aryl-assisted ionization mechanism free of involvement of solvent nucleophilicity, l=0,[1,2,11—13) one may expect that the $\log k$ values will be linearly correlated with the ionizing power scale Y_{OTs}. However, both the neophyl and related aryl-assisted solvol-



Scheme 1. The solvolysis mechanism of *threo*-1-methyl-2-phenylpropyl tosylate **2**.

yses display nonlinear plots when drawn against Y_{OTs}, with significant dispersion for various binary solvent mixtures.[1,13)] Schleyer, Bentley, and co-workers emphasized that the extended Winstein–Grunwald Equation 2 should be applied only to simple saturated alkyl substrates which do not yield resonance-stabilized carbenium ions.[9a)] Furthermore, they noted that Eq. 2 was based on assuming a k_s–k_c spectrum of mechanisms for simple alkyl substrates, and should not be used to correlate k_Δ solvolyses involving anchimeric assistance.

We have recently suggested that the dispersion behavior in the solvent correlations of neophyl tosylate **1H** may be characteristic of aryl-bridging, reflecting the charge-delocalization of the carbenium center by the aryl ring in the aryl-assisted transition state.[1,13,14)] In order to clarify the characteristic dispersion behavior of solvolyses of aryl-substituted substrates,[15,16)] we have undertaken intensive studies of the solvent effects of aryl-assisted solvolyses. The present paper deals with solvolyses of substituted *threo*-2-aryl-1-methylpropyl tosylates **2** (Chart 1), and introduces a new solvent effect correlation for aryl-assisted solvolyses.

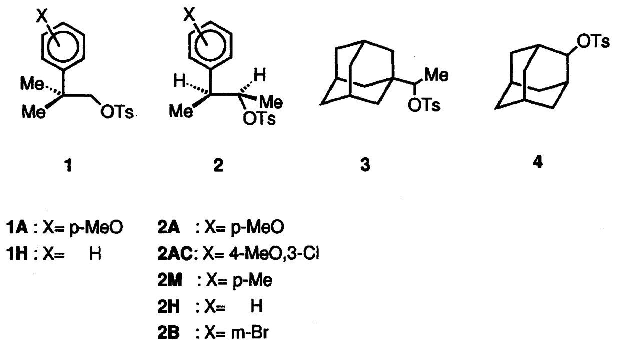


Chart 1.

Results

Solvolysis Data. Solvolysis rates of five *threo*-2-aryl-1-methylpropyl tosylates **2** having the ring-substituents *p*-methoxy- (**2A**), *p*-methyl- (**2M**), 3-chloro-4-methoxy- (**2AC**), hydrogen (**2H**), and *m*-bromo- (**2B**) were determined in a wide range of solvents, mostly by the conductimetric method. For comparison, the solvolysis rates of 1-(1-adamantyl)ethyl tosylate (**3**) were also determined under the same conditions. The data are summarized in Tables 1 and 2. The ionizing power scale Y_{OTs} and the nucleophilicity scale N_{OTs} parameters required for the correlations employed were mostly redetermined directly from solvolyses of 2-adamantyl tosylate (**4**) and methyl tosylate in this laboratory,[1,13,17—19)] and are listed in Table 3. Table 3 also includes an alternative set of solvent polarity parameters Y_Δ which are based on the solvolysis of *p*-methoxyneophyl tosylate (**1A**).[1)]

The Winstein–Grunwald Correlations. All the solvolysis data were analyzed by the simple Winstein–Grunwald Equation 3 as well as by its extended modification (Eq. 2).

$$\log(k/k_{80\mathrm{E}}) = mY_{\mathrm{OTs}}. \qquad (3)$$

The plots for tosylates **2A**, **2M**, and **2H** against Y_{OTs} are shown in Figs. 1, 2, and 3. A significant dispersion between different binary solvent mixtures is observed in all cases. The upward deviant behavior in aqueous TFE, EtOH–TFE, and AcOH–HCOOH mixtures is inconsistent with contribution from nucleophilic solvent assistance. The pattern of dispersion is essentially the same for tosylates **2A**, **2M**, **2AC**, and **2H** and those previously observed for the neophyl system,[1,13)] and we conclude that the dispersion in the mY plots is not due to nucleophilic solvent assistance.

Table 1. Rate Data for Solvolysis of *threo*-1-Methyl-2-phenylpropyl Tosylates (**2**)[a]

Solvent[b]	$10^5\ k_t/\mathrm{s}^{-1}$				
	p-MeO (**2A**) 25 °C	3-Cl,4-MeO (**2AC**) 45 °C	*p*-Me (**2M**) 45 °C	H (**2H**) 45 °C	*m*-Br (**2B**) 45 °C
EtOH	0.5173	0.3172	0.4259	0.094[c]	
90E	2.508	1.314	2.183	0.4799	
80E	5.768	3.063	6.379	1.188	0.1703[d]
70E	10.34	5.635	13.74	2.620	0.2982[d]
60E	17.47	9.368	27.02	5.383	0.4723
50E	30.57	15.68	54.25	11.18	0.7735
40E	61.48	29.97	116.9	25.32	1.571
30E	152.2	65.39	305.7	71.01	3.522
MeOH	2.03	1.379	2.337	0.5058	0.1398[d]
80M	12.98	6.401	18.28	2.939	0.4758[d]
60M	44.9	21.37	81.03	15.02	0.9612
50M	80.7	37.93	162.7	31.31	1.812
80A	0.7632	0.4105	0.7622	0.123[c]	
70A	2.129	1.178	2.721	0.5124	
60A	5.554	2.837	8.093	1.490	0.1466
50A	13.87	6.815	21.88	4.605	0.3304
40A	34.89	16.29	61.86	16.66	1.061
30A	91.57	40.26	189.8	41.42	3.257
80ET	1.664	0.7669	1.307	0.2313	
60ET	5.320	2.074	4.499	0.5117	0.0351[d]
40ET	17.14	6.277	17.25	1.715	0.0718[d]
20ET	52.82	21.81	73.97	6.882	0.1381
TFE	166.0	71.95	313.9	29.27	0.4985
97Tw	146.7	56.83	275.0	28.68	0.4408[d]
80T	116.7	49.20	247.4	30.30	0.5264[d]
50T	112.7	52.01	282.5	35.81	0.9059
40T	119.5		296.2		
30T	136.5	76.32	360.4	64.20	2.031
97HFIPw	1658	578.9	7334[d]	793.1	
50HFIP	314.8		849.3	113.0	
AcOH[e]	0.577[f] 0.552[h]			0.238[g]	
75AF	26.47			3.150	
50AF	115.5				
25AF	293.2				
HCOOH	593			228.0	
50D				3.839	
80AN	2.739	1.602	3.583	0.5464	
60AN	9.236	6.119	16.90	2.881	0.3449[d]
50AN	19.39	10.82	34.43	7.160	0.4494

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, A=acetone, D=dioxane, M=methanol, AN=acetonitrile, T=TFE=2,2,2-trifluoroethanol, HFIP=1,1,1,3,3,3-hexafluoro-2-propanol, AF=acetic acid-formic acid mixtures (e.g., 75AF=75 : 25 (v/v) acetic acid–formic acid mixture), and ET=ethanol–TFE mixtures (e.g., 80ET=80 : 20 (v/v) EtOH–TFE mixture). Suffix w means weight percent (w/w). c) Calculated from rate at 65 °C based on correlation between $\log k_{45^\circ\mathrm{C}}$ and $\log k_{65^\circ\mathrm{C}}$ in aqueous ethanol solvents. d) Extrapolated from data at other temperatures. e) Titrimetrically determined. f) Ref. 29. g) S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber, and J. Corse, *J. Am. Chem. Soc.*, **74**, 1113 (1952). h) Ref. 20b.

The results of correlations with Eq. 2 based on the conventional Y_{OTs} and N_{OTs} parameters are summarized in Table 4. Correlations vs. the Y_{OTs} parameter alone (Eq. 3) were poor for the aryl-assisted solvolyses of Entries 1—5 (R=0.95—0.97; SD=±0.19—0.25). It is evident that the strong aryl-assistance results in enhanced dispersion in the Y_{OTs} plot for varying binary solvent mixtures and with a reduced m value.

All the solvolyses of tosylates **2** except for **2B** (Fig. 4) have yielded negative lN terms in correlations with Eq. 2. These could be ascribed to nucleophilic assistance by the fixed intramolecular aryl group rather than

Table 2. Solvolysis Rates of 1-(1-Adamantyl)ethyl Tosylate (**3**)[a]

Solvent[b]	$10^5\ k/\mathrm{s}^{-1}$ 25 °C	$10^5\ k/\mathrm{s}^{-1}$ 45 °C	$10^5\ k/\mathrm{s}^{-1}$ (Temp/°C)		$\Delta H^{\ddagger}_{25\,^\circ\mathrm{C}}$[c] kcal mol^{-1}	$\Delta S^{\ddagger}_{25\,^\circ\mathrm{C}}$[c] e.u.
EtOH	0.00326[d]	0.0660[d]	0.4967(60),	17.07(90)[e]	27.8	0.3
90E	0.0247[d]	0.4267	16.58(75)		26.3	−0.7
80E	0.0907[d] 0.079[d,f,g]	1.382	9.196(60),	46.67(75)	25.2	−1.5
70E	0.244[d] 0.23[f]	3.637	116.9(75)		24.9	−0.8
60E	0.693[d] 0.67[d,f]	9.165	98.80(65),	253.2(75)	23.9	−1.9
50E	1.599	23.56			24.8	2.6
40E	6.401	75.35			22.6	−1.8
30E	39.54	328.4			19.4	−9.2
MeOH	0.0225[d]	0.4209	5.696(65),[e]	18.15(75)[e]	27.1	1.8
80M	0.3458	4.950	59.18(65)[e]		25.2	0.8
60M	3.359	42.02			23.2	−1.1
50M	10.17	119.8			22.7	−0.8
80A	0.0122[d]	0.2200	9.046(75)[e]		26.7	−0.7
70A	0.05035[d]	0.8769	11.09(65),[e]	34.45(75)[e]	26.4	1.1
60A	0.228[d]	3.260	0.9007(35)		24.5	−2.3
50A	0.9723	12.06			23.1	−3.9
40A	4.236	50.03			22.7	−2.5
30A	21.75	204.7			20.5	−6.4
20A	102[f,h]	811.6				
80ET	0.0171[d]	0.261[d]	0.8986(55),	8.629(75)	25.1	−5.4
60ET	0.0631[d]	0.8213	7.896(65)		23.6	−7.8
40ET	0.2429	3.467			24.5	−2.2
20ET	1.448	17.89			23.1	−3.2
TFE	9.462	100.1			21.5	−4.9
97Tw	9.591,9.65[g]	95.74			21.1	−6.2
80T	9.943	107.2			21.8	−3.7
70Tw		130.2				
50T	14.02	168.7			22.9	0.5
50Tw		195.8				
40T	17.49	220.3			23.3	2.4
30T	24.44	301.9			23.1	2.4
97HFIPw	536.6 540[f,i]	3330[d]	37.55(0)		16.6	−13.2
50HFIP	54.60	437.6			19.0	−9.7
AcOH	0.0138[d,f,g]	0.309[j]	7.5(70)[g]			
75AF		8.006				
25AF		288				
HCOOH	88.82,75[f,g]	870.7			20.9	−2.3
90AN	0.0184[d]	0.2524	7.291(75)		24.1	−8.6
80AN	0.0901[d]	1.268	37.87(75)		24.3	−4.6
60AN	0.5510	9.135			25.9	4.2
50AN	1.439	23.37			25.7	5.4

a)b) See footnotes a and b of Table 1. c) 1 cal=4.184 J. d) Extrapolated from rate data at other temperatures. e) Determined by the ampoule technique with conductivity determination. f) Ref. 9b. g) Ref. 26a. h) Estimated from data for the mesylate. i) Spectrophotometrically determined. j) Titrimetrically determined.

by the solvent nucleophile in the aryl-assisted systems or to more significant nucleophilic solvent attack in the solvolysis of **4** than in those of **2**. We believe, however, that the negative l value arises from an artifact in the correlation.

When we applied the similarity comparison analysis with a different reference Y scale (designated Y_Δ) based on the solvolysis of p-methoxyneophyl tosylate **1A** (Eq. 4),[1,17]

$$\log{(k/k_{80\mathrm{E}})} = m'Y_\Delta, \tag{4}$$

Table 3. Solvent Parameters[a)]

Solvent[b)]	Y_{OTs} 2-Adamantyl OTs 25 °C	N_{OTs}[c)]	Y_{Δ} *p*-Methoxyneophyl OTs 45 °C
EtOH	−1.75	0.00	−0.790
90E	−0.62	0.03	−0.281
80E	**0.00**	**0.00**	0.000
70E	(0.49)	−0.05	0.223
60E	(0.95)	−0.09	0.394
50E	1.37	−0.11	0.612
40E	1.97	−0.22	0.833
30E	2.67	−0.31	1.117
20E	3.32	−0.34	1.418
MeOH	(−0.92)	−0.04	−0.368
80M	(0.47)	−0.05	0.298
60M	(1.52)	−0.13	0.735
50M	(2.00)	−0.19	0.928
80A	(−0.95)	−0.42	−0.823
70A	−0.20	−0.38	−0.454
60A	0.45	−0.34	−0.120
50A	(1.09)	−0.35	0.199
40A	1.75	−0.39	0.546
30A	2.43	−0.40	0.909
20A	3.05	−0.44	1.237
80ET	−1.18	−0.19	−0.393
60ET	−0.44	−0.55	0.015
40ET	0.21	−1.01	0.454
20ET	0.98	−1.72	0.824
TFE	1.76	−3.0	1.277
97Tw	1.83	−2.79	1.123
80T	1.92	−1.90	1.092
70Tw	2.00	−1.20	1.068
50T	(2.15)	−1.14	1.081
50Tw	(2.19)	−0.95	1.085
40T	2.27	−0.92	1.111
30T	2.43	−0.80	1.152
97HFIPw	3.61	−4.27	2.088
50HFIP	2.51	−1.78	1.424
AcOH	−0.61	−2.35	−0.325
75AF	0.70	−2.35	0.551
50AF	1.62	−2.35	1.073
25AF	2.33	−2.35	1.423
HCOOH	3.04	−2.35	1.706
80D	−1.30	−0.29	−0.833
60D	0.25	−0.26	−0.111
50D	1.03	−0.29	0.311
90AN	−0.80	−1.24	−0.828
80AN	−0.01	−0.90	−0.408
60AN	0.89	−0.64	0.091
50AN	1.31	−0.57	0.320

a) Data taken from Refs. 1, 13, 17, and 18. b) See footnote b of Table 1. c) $N_{\mathrm{OTs}}=\log(k/k_{80\mathrm{E}})_{\mathrm{MeOTs}}$ (at 50 °C)$-0.3Y_{\mathrm{OTs}}$. d) $Y_{\Delta}=\log(k/k_{80\mathrm{E}})_{p\text{-Methoxyneophyl OTs}}$ (at 45 °C).

we obtained distinctly better correlations (R>0.990; SD<0.14) for substrates **1A, 1H, 2A, 2AC,** and **2M** (Entries 1—5 in Table 5) than in their correlations against Y_{OTs}. However, Eq. 4 does not give a good correlation for the unsubstituted **2H** (Entry 6) and the deviation is larger for the *m*-bromo tosylate **2B** ($R<0.9$; SD>0.3), as shown in Table 5. The plots of $\log k$ for **2A, 2M,** and **2H** against Y_{Δ} and Y_{OTs} are compared in Figs. 1, 2, and 3. There is a considerable difference in the goodness of fit of the correlations with Eq. 4 between the activated substrates (Entries 1—5 in Table 5) which show a better fit and the unsubstituted **2H**. The improved correlation with Y_{Δ} for these substrates enables us to use the goodness of fit as a probe which reasonably distinguishes between the k_{c} and k_{Δ} character of transition states. The present results are qual-

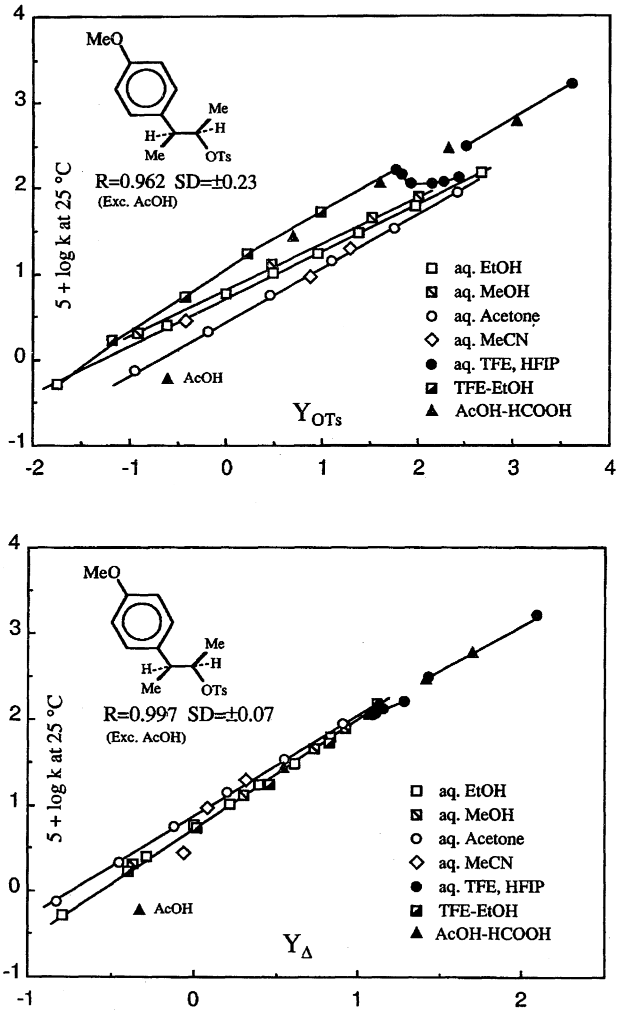


Fig. 1. The mY_{OTs} and $m'Y_\Delta$ plots for the solvolysis of *threo*-2-(*p*-methoxyphenyl)-1-methylpropyl tosylate **2A** at 25 °C.

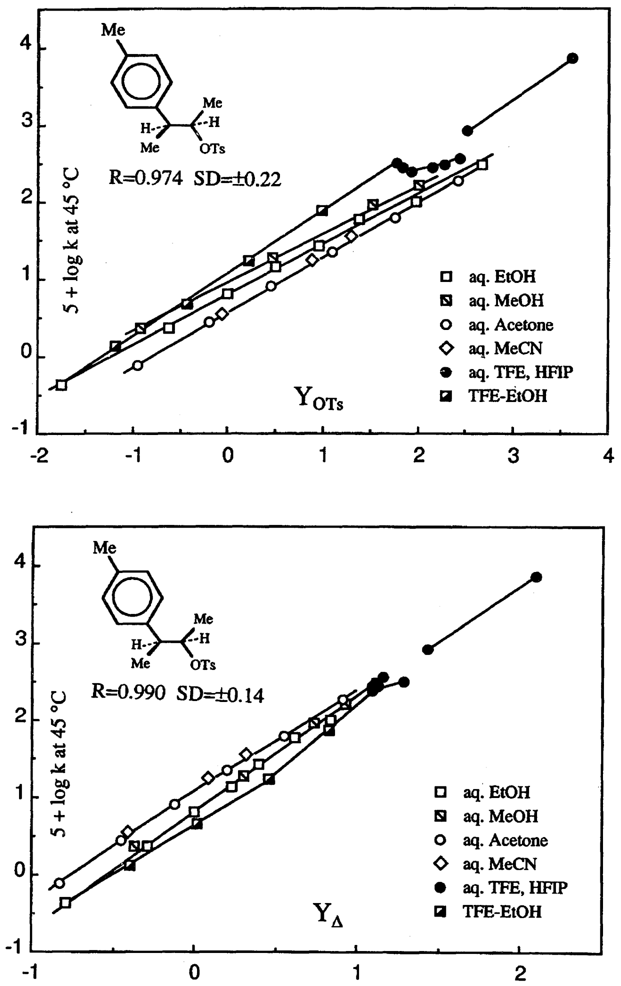


Fig. 2. The mY_{OTs} and $m'Y_\Delta$ plots for the solvolysis of *threo*-2-(*p*-methylphenyl)-1-methylpropyl tosylate **2M** at 45 °C.

itatively consistent in many cases with what Roberts envisaged in his recognition procedure.[12)]

The pronounced aryl-assistance leads to better correlations with the Y_Δ scale for the solvolysis of the methoxy substituted tosylate **2A**, and to somewhat less good correlations for the solvolysis of the 4-methyl derivative **2M**, vs. Y_Δ. In contrast, correlations vs. the Y_{OTs} scale are better than vs. the Y_Δ scale ($R<0.97$) for the unsubstituted **2H**. The closer the similarity of the transition state structure of a substrate investigated to that of the reference substrate, the better the linearity of the correlation behavior, and the higher is the confidence in it. The solvolyses of **2M** and **2H** even result in better correlations with Eq. 4 when the unsubstituted-neophyl-based Y_{neo} scale rather than the *p*-methoxyneophyl-based Y_Δ scale is used. There seems to be a gradation in the similarity of the transition state structures or in the extent of anchimeric assistance in the solvolyses of **2A, 2M, 2AC,** and **2H**.

Finally, we introduce here a new similarity comparison analysis (Eq. 5).

$$\log(k/k_{80E}) = m_c Y_{OTs} + m_\Delta Y_\Delta, \qquad (5)$$

where $\log(k/k_{80E})$ values for a given substrate are correlated with a linear combination of Y_{OTs} and Y_Δ. The solvent effect on the solvolysis of **4** and **1A** tosylates provides a model of the two extreme mechanistic routes k_c and k_Δ, respectively, for compounds undergoing partial or complete anchimeric assistance. The adjustable blending parameters m_c and m_Δ reveal the extent to which any substrate approaches 2-adamantyl ($m_\Delta=0$) or *p*-methoxyneophyl ($m_c=0$) in behavior. Equation 5 can be applied quite successfully with an extremely high precision ($R>0.996$ and $SD<0.09$), to all the solvolyses, excluding that of **2B**, as summarized in Table 6. The excellent linear correlations with Eq. 5 are shown for **2M** and **2H** in Figs. 5 and 6. Since the point for AcOH in Fig. 1 shows a large deviation, probably due to the well-known ion-pair return involved,[20)] the data in glacial AcOH for the aryl-assisted route were excluded from the present correlation analysis.

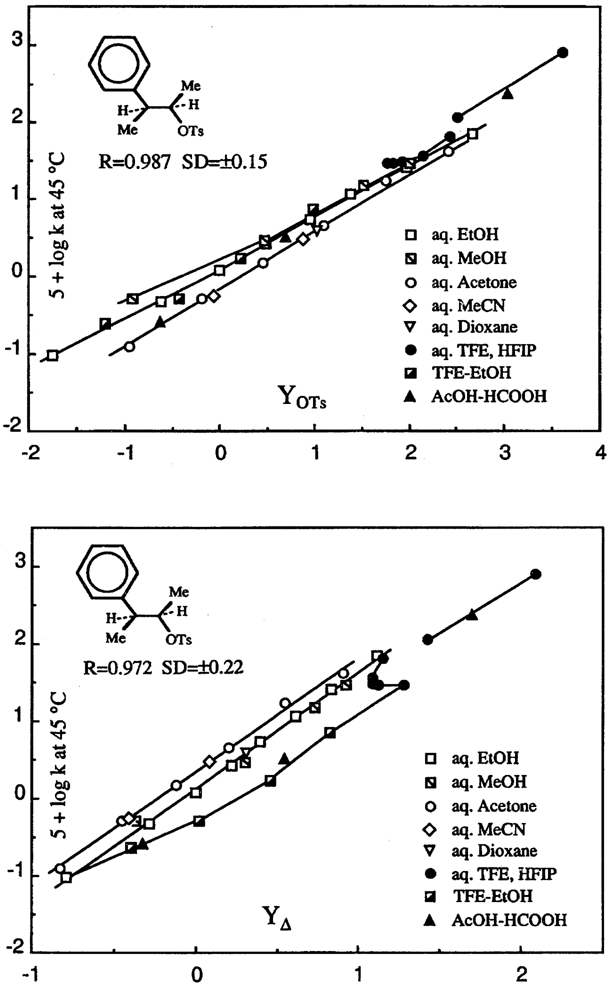


Fig. 3. The mY_{OTs} and $m'Y_{\Delta}$ plots for the solvolysis of *threo*-1-methyl-2-phenylpropyl tosylate **2H** at 45 °C.

The m_c and m_{Δ} values change in a complementary manner with the change of the substrate. The m_c value increases from 0.00 for **1A** to 1.00 for **4**, whereas the m_{Δ} value decreases in parallel from 1.00 to 0.0. The blending parameter for the correlation vs. Y_{Δ} relative to that vs. Y_{OTs} for any given substrate, $m_{\Delta}/(m_{\Delta}+m_c)$,[21] varies monotonically in the range from 1.00 for **1A** to 0.00 for **4** — the limiting k_c reference. This is in the direction expected if the dispersion in the Y_{OTs} plot becomes less pronounced for a system showing less significant anchimeric assistance. The substrates solvolyzed by an effective aryl-assisted mechanism display high $m_{\Delta}/\underline{m}$ values (where $\underline{m}=m_c+m_{\Delta}$), which are close to unity with acceptable conformity and a comparable precision for both Eqs. 4 and 5. It is noteworthy that Eq. 5 can be applicable with an equal precision to all the solvolyses, irrespective of the fact that m_c or m_{Δ} values are variable.

Neither the use of Eq. 4, nor of Eq. 5 improves the correlation for **2B**. However, the three-parameter equation: $\log{(k/k_{80\mathrm{E}})}=0.61Y_{\mathrm{OTs}}-0.02Y_{\Delta}+0.20N_{\mathrm{OTs}}$ correlates the data successfully, excluding the strongly nucleophilic solvents. This suggests that **2B** solvolyzes mainly by a simple k_s pathway, presumably of a concerted $\mathrm{S_N}2$ mechanism. The downward deviations for less nucleophilic solvents in the mY_{OTs} plot of Fig. 4 are compatible with a significant involvement of solvent nucleophilicity, and there is no contribution of a concomitant aryl-assisted pathway since $m_{\Delta}\approx 0$ in the solvolysis of **2B**.

Discussion

According to the mechanistic framework of Winstein,[7,11] solvolysis reactions are either nucleophilically solvent assisted (k_s) or anchimerically assisted (k_{Δ}), with k_c representing the hypothetical limit which is approached when nucleophilic solvent assistance and anchimeric assistance approach zero.[9a] The Winstein–Grunwald Eq. 3 using Y_{OTs} is considered to apply very precisely to solvolyses of the limiting k_c class and therefore the observed precise conformity allows us to explicitly assign the k_c mechanism to the systems studied. From the precise fit to Eq. 3 with Y_{OTs}, the solvolysis of **3** is assigned as a limiting k_c mechanism,[9b] whereas the less precise fit of **2A, 2AC, 2M,** and **1H** does not enable us to assign the k_c mechanism for them. On the other hand, the deviations from linearity in the $\log k$ vs. Y_{Δ} plots of Eq. 4 indicate that **2H** and **3** do not solvolyze by an anchimeric assistance mechanism. This approach, based on the precise conformity to either Eq. 3 or Eq. 4, seems to provide a clear-cut mechanistic division into k_c and/or k_{Δ} categories, respectively, although it is not easy to draw a borderline between them. Nevertheless, all the Entries in Table 6 except for **2B** can be correlated with the dual parameter Eq. 5 in equal uniformity and an extremely high precision. A simultaneous operation of the two competing pathways in Scheme 1 should not lead to such an exact fit to a linear correlation with Eq. 5, whereas the observation of any linear solvent effect relationship should indicate the operation of a single mechanism throughout the whole series of solvents examined. Thus, the conclusions drawn from the single parameter mY treatment with either Eq. 3 or Eq. 4 are often inconsistent with conclusions based on the excellent fit to Eq. 5. It is therefore remarkable that Eq. 5 can apply equally precisely to all the k_{Δ} solvolyses. The criterion of acceptable conformity of correlations applied here, i.e., SD<0.09 and R>0.996, is high. This is done on purpose, since the validity of mechanistic conclusions based particularly on Eq. 5 relies heavily upon the precision level of the fit, which should overweigh the ordinary criterion of fit of correlations with a single Y parameter scale.

The substituent effect analysis reveals that the solvolysis of the family of compounds **2** involves a clear mechanistic changeover from aryl-assisted to aryl-unassisted route with the change in substituent. The correlational

Table 4. Correlation Analysis of Solvent Effects on Solvolyses according to Eq. 2: $\log(k/k_{80E}) = mY_{OTs} + lN_{OTs}$

No.	R in ROTs	°C	m	l	$n^{a)}$	$R^{b)}$	SD$^{c)}$
1.	*p*-Methoxyneophyl	45	0.47	−0.15	49	0.969	±0.19
			0.50			0.953	±0.23
2.	2-(*p*-Methoxyphenyl)-1-methylpropyl	25	0.55	−0.18	37	0.981	±0.17
			0.63			0.962	±0.23
3.	2-(3-Chloro-4-methoxyphenyl)-1-methylpropyl	45	0.53	−0.13	31	0.980	±0.16
			0.58			0.969	±0.19
4.	Neophyl	45	0.60	−0.16	46	0.983	±0.19
			0.68			0.968	±0.25
5.	2-(*p*-Methylphenyl)-1-methylpropyl	45	0.66	−0.19	33	0.988	±0.16
			0.74			0.974	±0.22
6.	1-Methyl-2-phenylpropyl	45	0.70	−0.06	35	0.989	±0.14
			0.73			0.987	±0.15
7.	2-(*m*-Bromophenyl)-1-methylpropyl$^{d)}$	45	0.60	0.21	23	0.977	±0.11
			0.55			0.918	±0.21
8.	1-(1-Adamantyl)ethyl	45	0.89	−0.04	41	0.996	±0.11
			0.90			0.996	±0.12
9.	2-Adamantyl	25	1.00	0.00		(Definition)	

a) Number of data points. b) Correlation coefficient. c) Standard deviation. d) Excluding MeOH and 80M.

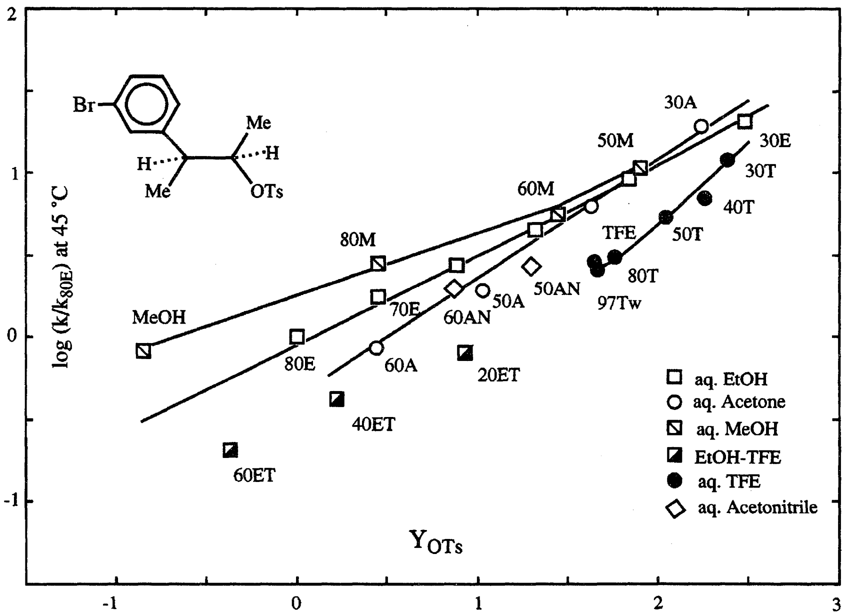


Fig. 4. The mY_{OTs} plot for the solvolysis of *threo*-2-(*m*-bromophenyl)-1-methylpropyl tosylate **2B** at 45 °C.

Table 5. Correlation Analysis of Solvent Effects on Solvolyses according to Eq. 4: $\log(k/k_{80E}) = m'Y_{\Delta}$

No.	R in ROTs	°C	m'	$n^{a)}$	$R^{b)}$	SD$^{c)}$
1.	*p*-Methoxyneophyl	45	1.00		(Definition)	
2.	2-(*p*-Methoxyphenyl)-1-methylpropyl	25	1.18	37	0.997	±0.07
3.	2-(3-Chloro-4-methoxyphenyl)-1-methylpropyl	45	1.12	31	0.991	±0.10
4.	Neophyl	45	1.23	45	0.995	±0.09
5.	2-(*p*-Methylphenyl)-1-methylpropyl	45	1.40	33	0.990	±0.14
6.	1-Methyl-2-phenylpropyl	45	1.32	35	0.972	±0.22
7.	2-(*m*-Bromophenyl)-1-methylpropyl$^{d)}$	45	0.76	23	0.65	±0.39
8.	1-(1-Adamantyl)ethyl	45	1.60	41	0.966	±0.32
9.	2-Adamantyl	25	1.82	49	0.953	±0.45

a)b)c) See footnotes a, b, and c of Table 4. d) Excluding MeOH and 80M. Including N_{OTs} term, $m'=1.20$ and $l=0.43$ ($R=0.88$ and SD$=\pm0.26$).

Table 6. Correlation Analysis of Solvent Effects on Solvolyses according to Eq. 5: $\log(k/k_{80E}) = m_c Y_{OTs} + m_\Delta Y_\Delta$

No.	R in ROTs	°C	m_c	m_Δ	$n^{a)}$	$R^{b)}$	SD$^{c)}$
1.	*p*-Methoxyneophyl	45	0.00	1.00		(Definition)	
2.	2-(*p*-Methoxyphenyl)-1-methylpropyl	25	0.14	0.95	37	0.999	±0.04
3.	Neophyl	45	0.16	0.95	45	0.998	±0.06
4.	2-(3-Chloro-4-methoxyphenyl)-1-methylpropyl	45	0.20	0.77	31	0.998	±0.05
5.	2-(*p*-Methylphenyl)-1-methylpropyl	45	0.29	0.89	33	0.998	±0.06
6.	1-Methyl-2-phenylpropyl	45	0.46	0.52	35	0.996	±0.09
			0.52	0.47	$32^{d)}$	0.997	±0.07
7.	2-(*m*-Bromophenyl)-1-methylpropyl$^{e)}$	45	0.79	−0.54	23	0.951	±0.17
8.	1-(1-Adamantyl)ethyl	45	0.72	0.36	41	0.998	±0.08
9.	2-Adamantyl	25	1.00	0.00		(Definition)	

a)b)c) See footnotes a, b, and c of Table 4. d) Excluding data in EtOH, 90E, and MeOH. e) Excluding data in MeOH and 80M.

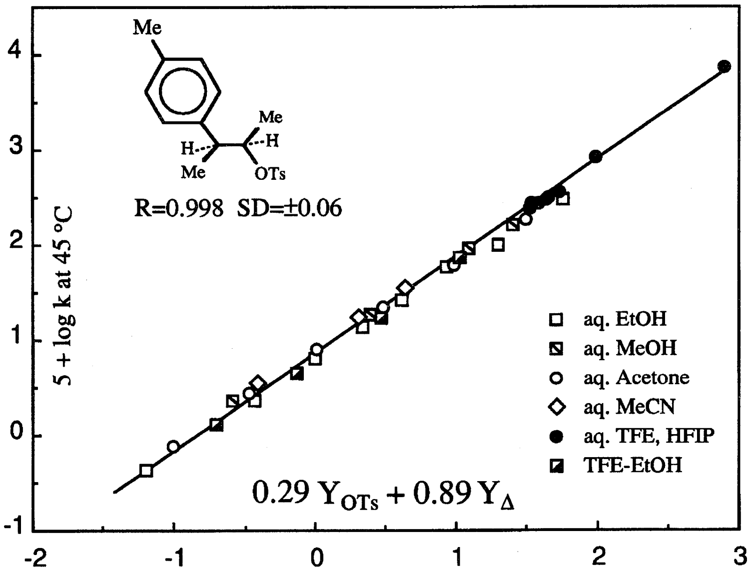


Fig. 5. The ($m_c Y_{OTs}+m_\Delta Y_\Delta$) plot for the solvolysis of *threo*-2-(*p*-methyphenyl)-1-methylpropyl tosylate **2M** at 45 °C.

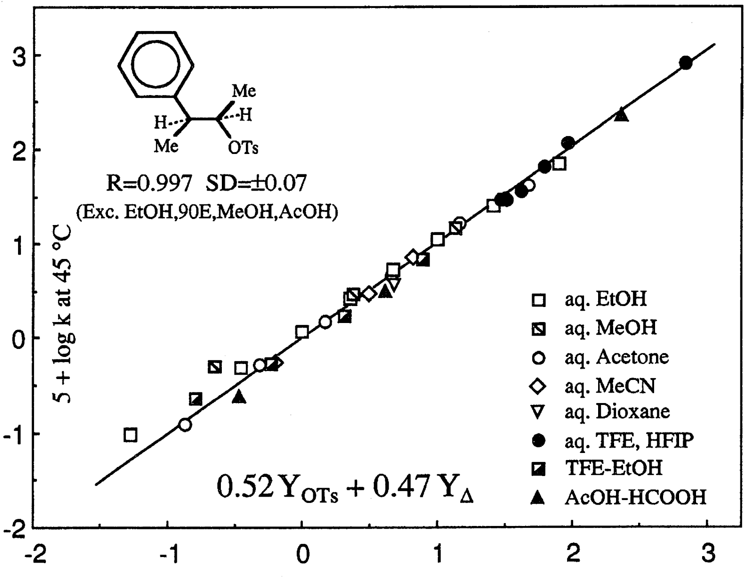
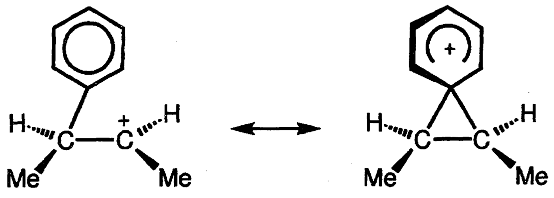


Fig. 6. The ($m_c Y_{OTs}+m_\Delta Y_\Delta$) plot for the solvolysis of *threo*-1-methyl-2-phenylpropyl tosylate **2H** at 45 °C.

indices for the substituent effects in typical solvents are summarized in Table 7. Clearly, the electron-donating derivatives in almost all solvents, and **2H** in less nucleophilic solvents, react by the aryl-assisted k_Δ pathway. The aryl-unassisted (k_s) pathway (Scheme 1) depends significantly upon the solvent nucleophilicity, and the reaction of electron-withdrawing derivatives could have proceeded by this pathway. However, the correlation for **2H** with Eq. 5 is only slightly improved (R=0.997 and SD=0.07) by excluding the strongly nucleophilic solvents EtOH, MeOH, and 90% EtOH (Table 6). We therefore believe that the aryl-assisted process is still the exclusive pathway in the solvolysis of **2H**, even if the results of the correlation are not sufficiently conclusive to exclude competition by the k_s pathway, particularly in very strongly nucleophilic but very weakly ionizing solvents. On the other hand, Eq. 5 clearly fails to correlate linearly the solvent effect for **2B**, which in our opinion solvolyzes almost exclusively through the k_s pathway, even though the k_Δ mechanism (pathway) could compete with dominant k_s mechanism (pathway) in only extremely less or non-nucleophilic solvents. The solvolyses of derivatives **2**, which are more reactive than **2H**, are ascribed to the aryl-assisted process, which is statistically distinguishable from the competing k_s route.

As already pointed out, the dispersion behavior of compounds **1**, **2**, and related β-arylalkyl substrates undoubtedly arises from aryl-bridging in the transition state,[1,13] and is a consequence of positive charge-delocalization into the aryl ring. The dispersal in plots vs. the ionizing-power parameter should reflect different stabilizing effects of binary solvent mixtures on a delocalized carbocation compared with a simple localized carbocation.

The intermediate in aryl-assisted solvolyses may be represented (Fig. 7) as a hybrid of structures (**5**) and (**6**), which illustrate the hypothetical open and bridged (phenonium) ions, respectively. The transition state for the solvolysis of **1A** and **2A** may be modeled by the canonical structure **6**, whereas that for **2M** is best modeled as a resonance hybrid of **5** and **6**. The assistance becomes less important for **2H** and the structure of the transition state can be approximated by the open cation structure **5**. The anchimeric assistance mechanism may be regarded as an intramolecular concerted displacement by the aryl group serving as a carbon-nucleophile, and therefore the change described in the structure of the transition state could be attributed to a shift of the transition state relative to the intermediate along the reaction coordinate. However, it is conceivable that the movement of the transition state along the reaction coordinate is not very important within the closely related system, e.g., a series of substituted compounds giving a linear substituent effect relationship. The intermediate cation considered here also does not necessarily have an extremely unsymmetrical structure; the intermediate in the solvolysis of **2** should have the so-called symmetric phenonium ion structure. The accurate structure of phenonium ion can now be determined computationally,[22] and the optimized structure may be a good model of the transition state of the anchimerically assisted solvolysis. The recently calculated MP2(FU)/6-31G* optimized structures of the phenonium ions derived from **2A** and **2H**[23] are shown in Figs. 8 and 9. The degree of charge delocalization in a phenonium ion can be deduced by the NPA charge distribution between the aromatic and non-aromatic moieties (Table 8). We find an extensive intrinsic charge delocalization in the phenonium ion derived from **2H** and remarkably higher delocalization in the p-methoxy-substituted ion derived from **2A**. Similar results are seen for ethylenephenonium ions calculated by Schleyer et al.[22] In the optimized structures of neophyl ions, for which the bridged cations are obtained as intermediates (not transition states), and of α-methylphenonium ions, the bridging and delocalization are similarly significant, but the optimized structures of the ions are appreciably unsymmetrical.[23] The degree of delocalization in the phenonium ions appears to be comparable with or even higher, though it is substituent-dependent, than



5 **6**

Fig. 7. The open k_c cation **5** and phenonium (bridged) ion **6** for the 2-phenylalkyl system.

Table 7. Substituent Effect on the Solvolysis of *threo*-2-Aryl-1-methylpropyl Brosylates

Solvent	Temp/°C	ρ_Δ	r_Δ	ρ_s	$\%Fk_\Delta$[a)]	$\bar{\sigma}$[b)]
AcOH[c)]	75	−3.36	0.56	−1.05	79%	0.25
80E[c)]	45	−3.71	0.54	−0.75	72%	0.05
97Tw[d)]	45	−4.18	0.42		100%	0.6

a) For the unsubstituted derivative. b) $\bar{\sigma}$-value at $Fk_\Delta=k_s$. c) Ref. 4. d) Unpublished result.

Table 8. Charges of Mulliken Population Analysis (MPA) and Natural Population Analysis (NPA) for the *threo*-1-Methyl-2-phenylpropyl Cations Calculated at a MP2(FU)/6-31G* Level

	p-MeO-substituted ion		Unsubstituted ion	
Atom[a)]	MPA	NPA	MPA	NPA
C1	−0.227	−0.217	−0.233	−0.190
C2	0.191	0.226	0.183	0.204
C3	0.002	−0.058	0.031	−0.011
C4	0.535	0.591	0.170	0.222
C5	−0.040	−0.129	0.038	−0.013
C6	0.199	0.267	0.176	0.211
O9	−0.614	−0.572		
C12,C13	0.144	0.153	0.179	0.193
C14,C15	0.120	0.084	0.139	0.096
C24	0.426	0.416		
Ar[b)]	0.473	0.525	0.365	0.423
Non-Ar[c)]	0.527	0.475	0.635	0.577

a) The numbering scheme is given in Figs. 8 and 9. Total charge on each carbon with hydrogens summed into heavy atom. b) Total charge in the aromatic moiety. c) Total charge in the non-aromatic moiety.

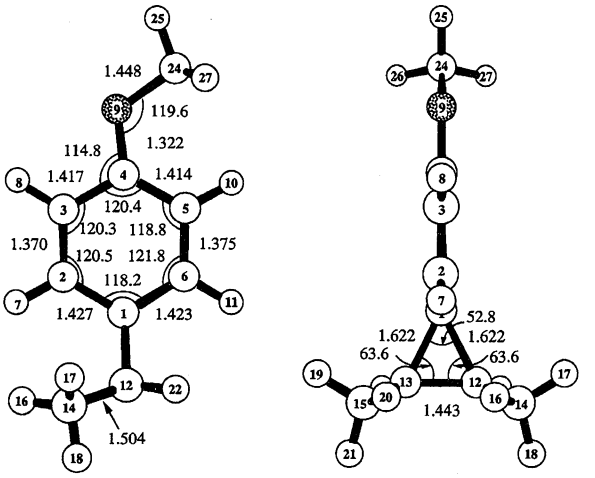


Fig. 8. Geometric parameters for MP2(FU)/6-31G* optimized structures of the phenonium ions derived from **2A**.

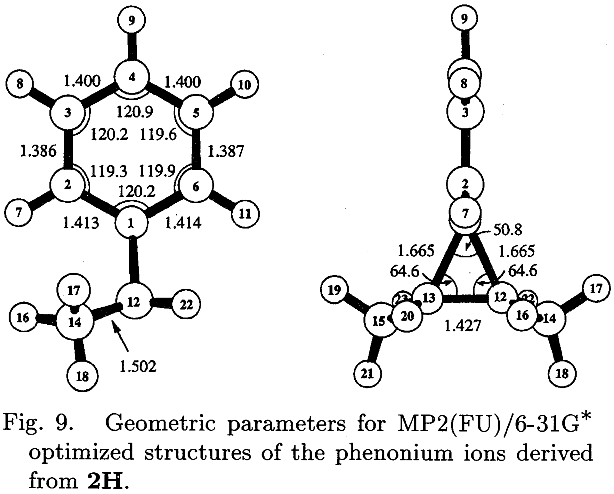


Fig. 9. Geometric parameters for MP2(FU)/6-31G* optimized structures of the phenonium ions derived from **2H**.

the delocalization in the benzylic carbocations.[25)] The change in the degree of charge delocalization and the degree of bridging (or aryl-assistance) in the phenonium ion intermediates may be reflected in the solvation of the solvolysis transition state as well as in that of the intermediate phenonium ion.

The degree of anchimeric assistance can be reasonably assessed by Eq. 5 using the blending parameter $m_\Delta/\underline{m}$, where $\underline{m}=m_c+m_\Delta$.[21)] This parameter can be applied to characterize a wider set of aryl-assisted solvolyses; several examples are given in Table 9. The $m_\Delta/\underline{m}$ value varies continuously from 1.0 for **1A** which reacts by a synchronous assisted process, via a reduced value for weakly bridging **2H**, to the extreme value of 0 for **4** — the limiting k_c reference. In closely related solvolyses, 2-(*p*-methoxyphenyl)cyclopentyl tosylate shows an $m_\Delta/\underline{m}$ value of 0.84 comparable to that for the solvolysis of **1H**, while 2-(*p*-methoxyphenyl)-1-methylethyl tosylate shows low assistance resembling **2M**.[25)] Intermediate $m_\Delta/\underline{m}$ values are obtained for the solvolyses of **2M**, **2H** and for the well-known k_Δ solvolysis of benzonorbornen-2-*exo*-yl tosylate, where the mechanisms should not closely resemble either mechanism of one of the model substrates. Even lower $m_\Delta/\underline{m}$ values of 0.3—0.5 are obtained for **2H** and **3**. **2H** reacts by the k_Δ mechanism similarly to its neophyl analogues. For tosylate **3** which lacks an aryl group, the appreciable size of the $m_\Delta/\underline{m}$ value lends support for a mechanism involving alkyl(σ)-assistance at the transition state, as suggested by the formation of isomerized products.[26)]

The k_c–k_Δ–k_s Mechanistic Spectra. Potential Energy Surface Diagrams. The continuous change in the $m_\Delta/\underline{m}$ value argues for the existence of a mechanistic spectrum for the compounds discussed here. The structure of the transition state in the solvolysis of **1A** and **2A** should resemble the bridged cation, while that

Table 9. Correlation Analysis of Solvent Effects on Solvolyses according to Eq. 5: $\log(k/k_{80E}) = m_c Y_{OTs} + m_\Delta Y_\Delta$

No.	R in ROTs	°C	m_c	m_Δ	$m_\Delta/\underline{m}$[a)]
1.	*p*-Methoxyneophyl	45	0.00	1.00	1.00
2.	2-(*p*-Methoxyphenyl)-1-methylpropyl	25	0.14	0.95	0.87
3.	Neophyl	45	0.16	0.95	0.86
4.	2-(*p*-Methoxyphenyl)cyclopentyl	45	0.16	0.83	0.84
5.	2-(3-Chloro-4-methoxyphenyl)-1-methylpropyl	45	0.20	0.77	0.79
6.	2-(*p*-Methoxyphenyl)-1-methylethyl	45	0.22	0.70	0.76
7.	2-(*p*-Methylphenyl)-1-methylpropyl	45	0.29	0.89	0.75
8.	Benzonorbornen-2-*exo*-yl	25	0.46	0.72	0.61
9.	1-Methyl-2-phenylpropyl	45	0.52	0.47	0.47
10.	1-(1-Adamantyl)ethyl	45	0.72	0.36	0.33
11.	(1-Phenylcyclobutyl)methyl	45	0.50	0.22	0.31
12.	(1-Phenylcyclopropyl)methyl	25	0.63	0.10	0.14
13.	2-Adamantyl	25	1.00	0.00	0.00

a) $m_\Delta/\underline{m} = m_\Delta/(m_c + m_\Delta)$.

for the solvolysis of **2H** should be even closer to that of the less delocalized and/or weakly bridged (i.e., open) cation. The incipient charge is more extensively transferred to the assisting aryl moiety on increasing the degree of anchimeric assistance in the transition state. This versatile character of the anchimerically assisted (k_Δ) process may be regarded as a "spectrum of k_c–k_Δ mechanisms", implying a progressive series of changes in its character. This mechanistic spectrum should be independent of the ordinary k_s–k_c spectrum for the substitution mechanism.

In spite of the potential complexity of the solvolytic processes, it is possible to rationalize the major features of the correlations on the basis of a k_s–k_c spectrum of mechanisms in which the extent of nucleophilic solvent assistance varies and a "k_Δ–k_c" spectrum of mechanisms in which the extent of anchimeric assistance varies.

The aryl-unassisted (k_s) pathway can be described by a three-dimensional potential energy surface diagram (PESD), known as the More O'Ferrall–Jencks diagram[27)] for the k_s–k_c spectrum (Fig. 10). The ionization process in the aryl-assisted (k_Δ) pathway can be described by the shaded surface in a PES-diagram. Each one of the discrete mechanistic spectra constitutes a discrete More O'Ferrall diagram (i.e., it lies in a PES in a different dimension) but both mechanistic spectra share a common axis toward the k_c extreme, a hypothetical limit where $m_\Delta = 0$ and/or $l = 0$. The k_Δ PESD is independent of that for the k_s–k_c spectrum but bor-

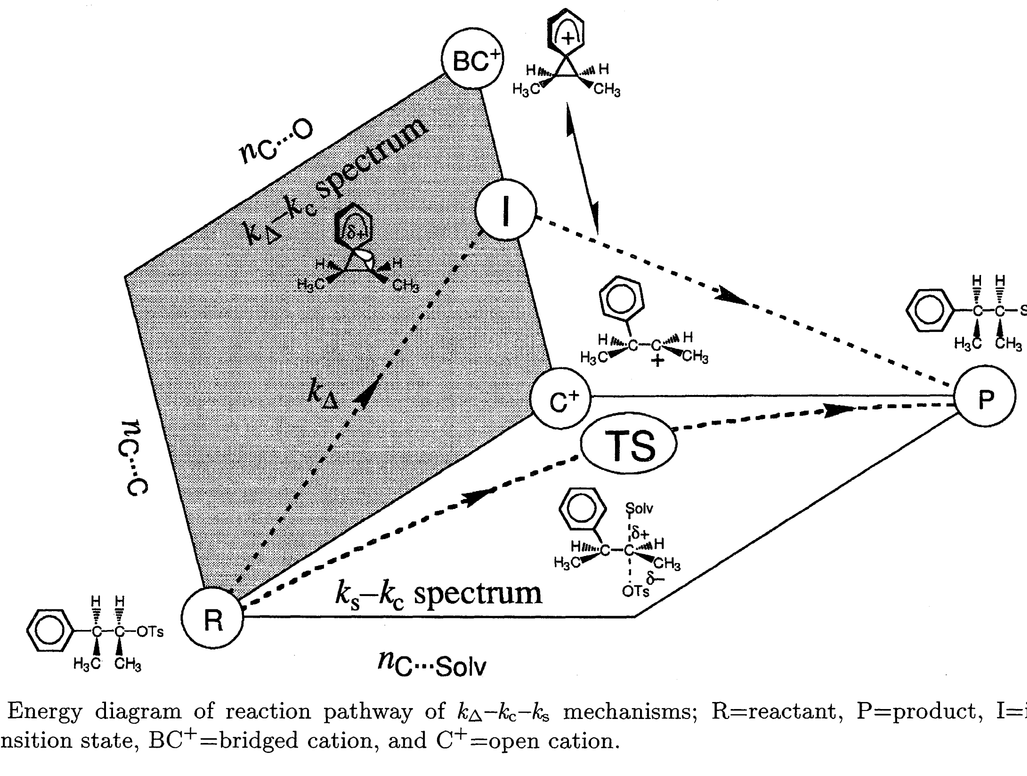


Fig. 10. Energy diagram of reaction pathway of k_Δ–k_c–k_s mechanisms; R=reactant, P=product, I=intermediate, TS=transition state, BC$^+$=bridged cation, and C$^+$=open cation.

ders it on the common axis which describes the leaving group bond fission. The k_c–k_Δ PESD can be described by the $n_{\mathrm{C}\cdots\mathrm{O}}$ axis for leaving group dissociation with the open carbocation in the corner, the other axis being the $n_{\mathrm{C}\cdots\mathrm{C}}$ bond length for the bridging process, with the phenonium ion at the corner. The aryl-assisted process lies in this surface, and the positions of the intermediate and the transition state may be quantified by the m_Δ and $\underline{m}$ values; the position of the transition state moves from the vicinity of the phenonium ion corner toward the open cation corner as the substituent becomes less electron-donating. This k_c–k_Δ diagram concerns only the nucleophilically (or solvolytically) limiting processes, and is independent of the horizontal axis of the C–Solv bond formation, as measured by the l parameter. The aryl-assisted process lies on the potential energy surface diagram, with the vertical axis having the precursor and the delocalized cation derived from it in the corners. In the solvolysis of **2H**, the vertical axis should become appreciably closer to the axis for localized (open) cation, but still the PESD's for the aryl-assisted and the aryl-unassisted (k_s) processes remain discrete. This fits the observed competition of k_s and aryl-assisted processes for solvolysis of **2H** in EtOH, 90E, and MeOH. The lower m_Δ value for the aliphatic precursor **3** suggests a k_Δ pathway close to the k_c axis toward the localized cation corner in the k_c–k_Δ PESD, and the rate-determining ionization process is free of nucleophilic solvent assistance due to a steric reason. Finally, the solvolysis of **2B** in almost all solvents belongs to the k_s–k_c diagram (clear surface in Fig. 10) without detectable aryl-assistance in the ionization process, since m_Δ=0.

We conclude that the present similarity comparison analysis based on Eq. 5 is quite successful for aryl-assisted solvolyses. Thus it enables us to assess precisely the varying extent of aryl-assistance in the transition state. Further investigations of a wider range of anchimerically assisted solvolyses are in progress.

Experimental

Materials: The tosylates were prepared by the Tipson procedure[28)] from the corresponding threo alcohols[4)] and p-toluenesulfonyl chloride in pyridine and were recrystallized from the appropriate solvent. The p-methoxy derivative **2A**, mp 46.0—47 °C, lit,[20b,29)] mp 49—50 °C, was recrystallized from ether–hexane. Anal. Found: C, 64.59; H, 6.58%. Calcd for $C_{18}H_{22}O_4S$: C, 64.59; H, 6.63%. 3-Chloro-4-methoxy derivative **2AC**, mp 83.0—83.5 °C, (from ether–hexane). Anal. Found: C, 58.59; H, 5.70%. Calcd for $C_{18}H_{21}O_4SCl$: C, 58.61; H, 5.74%. p-Methyl derivative **2M**, mp 44.7—45.2 °C, (from benzene–hexane). Anal. Found: C, 67.88; H, 6.91%. Calcd for $C_{18}H_{22}O_3S$: C, 67.90; H, 6.96%. Unsubstituted derivative **2H**, mp 47.2—47.5 °C, lit,[30)] mp 46—47 °C, mp 47—48 °C,[20b)] recrystallized from ether–hexane. Anal. Found: C, 67.05; H, 6.61%. Calcd for $C_{17}H_{20}O_3S$: C, 67.08; H, 6.62%. m-Bromo derivative **2B**, mp 36.5—37.5 °C. Anal. Found: C, 53.21; H, 5.00%. Calcd for $C_{17}H_{19}O_3SBr$: C, 53.27; H, 5.00%.

1-(1-Adamantly)ethyl tosylate **3** was synthesized from 1-(1-adamantyl)ethanol and tosyl chloride in pyridine and recrystallized from benzene–hexane, mp 121—122 °C, lit,[26a)] mp 117—118 °C. Anal. Found: C, 68.27; H, 7.79%. Calcd for $C_{19}H_{26}O_3S$: C, 68.23; H, 7.84%.

Anhydrous acetic acid, formic acid, acetone, acetonitrile, methanol, ethanol, 2,2,2-trifluoroethanol, and water were purified as described previously.[1,13,15,17,18,31)] 1,1,1,3,3,3-Hexafluoro-2-propanol (purity>99.99%) obtained from Central Glass Co., Ltd., was used without further purification. Dioxane was refluxed twice with sodium metal and the distillate was redistilled fractionally.

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

Kinetic Measurements: Solvolyses in aqueous binary solvents were followed conductimetrically as described earlier.[1,13,15,17,18)] Conductance measurements were made on a 10^{-3}—10^{-4} mol dm^{-3} solution of the starting tosylate in a thermostatted bath controlled to within ±0.01 °C. Solvolyses were followed by taking at least 100 conductivity readings (with a CM-50AT and CM-60S conductivity meter equipped with an interval unit and printer, Toa Electronics Ltd.) at appropriate intervals for 3 half-lives, and the infinity reading was taken after 10 half-lives. The precision of fit of the conductance readings to first-order kinetics over 3 half-lives was generally excellent ($R > 0.99998$). The solvolysis rates for the less reactive substrates were followed by using the sealed ampoule technique with conductivity determination as described previously.[17)] The acetolysis rates were determined by the ordinary titrimetric method using the ampoule technique for less reactive runs at high temperatures and the batch technique for relatively reactive runs.[31)] The experimental errors in respective runs were generally <1.0% and the reproducibility of the rate constants was ≦1.5%.

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