Bull. Chem. Soc. Jpn., ***68***, *2619—2628(1995)*

Solvent Effects on the Solvolysis of Benzyl Tosylates. Behavior of Derivatives with Electron-Donating Substituents

Mizue Fujio,* Toshihiro Susuki, Ken-ichi Yatsugi, Yoshihiro Saeki, Mutsuo Goto, Sung Hong Kim, Yutaka Tsuji, Zvi Rappoport, and Yuho Tsuno

Institute for Fundamental Research of Organic Chemistry, Kyushu University, Hakozaki, Fukuoka 812

(Received February 6, 1995)

Solvolysis rates of *p*-methylbenzyl and 3-bromo-4-(methylthio)benzyl *p*-toluenesulfonates were measured in a wide variety of solvents and the solvent effects were compared with those for less activated benzyl tosylates and other related benzylic substrates. Plots of the dual parameter Winstein–Grunwald Equation failed to give satisfactory correlations using the ordinary 2-adamantyl Y_{OTs} parameter. m Values close to unity for both derivatives were obtained but the linearity of the correlations was unsatisfactory. Although the high response (m value) to the solvent polarity and the low l value may indicate a nearly limiting mechanism, the pattern of dispersion observed in binary solvent mixtures cannot be interpreted in terms of nucleophilic solvent assistance. The use of the polarity scale Y_Δ derived from 2-methyl-2-(*p*-methoxyphenyl)propyl tosylate solvolysis instead of Y_{OTs} significantly improved the correlations. The dispersion can be ascribed to the varying solvation-desolvation interactions characteristic of highly delocalized cationic centers in binary solvent mixtures. We used extended similarity comparison analysis, $\log (k/k_{80\mathrm{E}}) = m_c Y_{\mathrm{OTs}} + m_\Delta Y_\Delta + (lN)$. Based on the resulting characteristic susceptibility parameters, the mechanisms of benzyl solvolysis and the structures of relevant benzylic solvolyses transition states are discussed.

Solvent effects on the solvolyses of benzyl tosylate (*p*-toluenesulfonate) and its ring-substituted derivatives by electron-withdrawing substituents (**1**) have been analyzed and discussed,[1,2] in terms of the Winstein–Grunwald–Schleyer–Bentley dual parameter Eq. 1,[3,4]

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

where the most widely used ionizing power and nucleophilicity parameters Y_{OTs} and N_{OTs} are derived from the solvolyses of 2-adamantyl tosylate and methyl tosylate, respectively.[4] While Eq. 1 had shown broad applicability for solvolyses of secondary and tertiary alkyl tosylates, an important limitation has been recently found in correlating the solvolyses of benzylic substrates.[5—13] We also reported that the solvolysis of benzyl tosylates gave no satisfactory correlations with the conventional Y_{OTs} and N_{OTs} parameters but showed significant dispersal of the mY plots for different binary solvent mixtures, with significantly low m values in these cases.[1] A more successful correlation with Eq. 1 was found by using an alternative kinetic solvent polarity scale, Y_{Bz}, based either on the solvolysis of α-(*t*-butyl)benzyl tosylate (**2**) or of neophyl(2-methyl-2-phenylpropyl) tosylate (**3**) (Chart 1). The solvolyses of the unsubstituted benzyl tosylate (**1H**) and *m*-chlorobenzyl tosylate (**1C**) were found to include a significant contribution of solvent nucleophilicity, with l values of 0.4 and of about 0.6, respectively.[1]

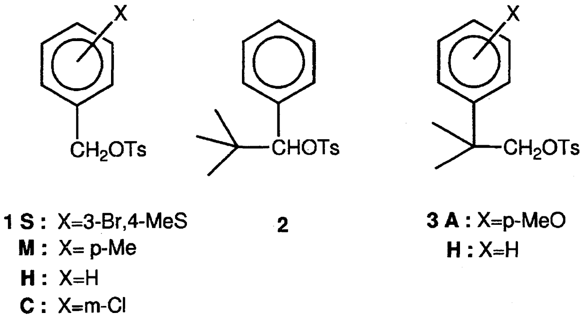

Chart 1.

Consequently, the dispersion of the $\log k$ vs. Y_{OTs} plots for various series of aqueous binary solvent mixtures could not be due to the solvent nucleophilicity but should reflect other factors associated with the benzylic $\mathrm{S_N1}$ ionization process. Similar dispersions have already been observed for solvolysis of other benzylic tosylates. For example, the neophyl tosylate (**3H**) solvolysis has a nonlinear response and a significant dispersion for binary solvent mixture series when correlated with the solvent polarity Y_{OTs} scale.[10,11] Identical behavior was observed in the solvolysis of 1-(*p*-methoxyphenyl)vinyl tosylate.[12] The m values in these cases are substantially lower than $m\approx1.0$, the value observed for S_N1 solvolyses of alkyl tosylates and significant dispersions are observed in the mY plots. These features are most likely due to a direct π-interaction between the charged carbocationic center and the α-aryl group.

In recent studies of the solvent effect on the solvolysis of benzyl tosylates, we have used the dual-parameter Eq. 2 using the solvent polarity (ionizing power) scale Y_{Bz},[1,2)]

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

Indeed, appreciably improved correlations for the unsubstituted benzyl tosylate **1H** and related benzyl tosylates were obtained by using the log k values based on the solvolysis of unsubstituted neophyl tosylate (**3H**) as a reference Y_{Bz} scale. Log k values for **2**[13)] can also serve as an appropriate reference scale for describing the behavior of benzylic precursors.

The precise mechanism of benzyl tosylate solvolysis has also been probed by analyzing the substituent effect.[14—16)] The Yukawa–Tsuno treatment,[17)] which gave a single smooth-curved correlation, led to interpretation in terms of an S_N1–S_N2 mechanistic shift on changing the ring substituent.[15,16)] There is a large variation in the extent of the solvent nucleophilicity contribution in the transition state with the nature of the aryl substituent.[1,2,15,16,18)] The difficulty in assigning a mechanism for the benzyl series is mainly in evaluating the extent of nucleophilic solvent involvement in the transition state. It is apparent that benzyl tosylates substituted by strongly electron-donating ring substituents solvolyze by a near-limiting k_c mechanism. Hence, their solvolysis rate should be almost exclusively dependent upon the solvent ionizing power and essentially independent of the solvent nucleophilicity. Consequently, solvent participation should be less important in solvolyses of the highly activated p-methyl (**1M**) and 3-bromo-4-methylthio (**1S**) derivatives than for the unsubstituted one, and for solvolytically more deactivated benzyl tosylates than **1H**. **1M** and **1S** should be appropriate candidates for examining the applicability of the Winstein–Grunwald treatment, and for examining the validity of the solvent polarity scales applied for correlating the solvolysis of benzyl tosylates. We therefore extended our studies to the solvolysis of these benzyl tosylates bearing strongly electron-donating substituents, which are anticipated to solvolyze by a limiting or a near-limiting k_c mechanism.

Results

Solvolysis rates of **1M** and **1S** were measured in a wide variety of solvents including binary aqueous mixtures with ethanol (E), methanol (M), acetone (A), dioxane (D), acetonitrile (AN), and 2,2,2-trifluoroethanol (TFE=T), and ethanol–TFE mixtures (ET). The high reactivity of these tosylates caused high solvolysis rates in highly polar solvents, which were inconvenient to follow by our conductimetric method. Unfortunately, accurate rate measurements in aqueous TFE mixtures, which are the most informative regarding the involvement of solvent nucleophilicity, were limited, but we were able to measure the rates of solvolysis in varying TFE–EtOH mixtures for the more reactive tosylate **1S**. The results are listed in Tables 1 and 2.

In Fig. 1, logarithmic rate constants for the solvolysis of **1M** at 0 °C are plotted against the 2-adamantyl tosylate-based Y_{OTs}. The plot shows extensive dispersal from linearity. The m_{EW} values are 0.80 for the aqueous ethanol series and $m_{\mathrm{AW}}=1.02$ for the aqueous acetone series; more important, there is a significant gap of 0.56 units between the interpolated log k values at $Y_{\mathrm{OTs}}=0$. The points for less nucleophilic, aqueous TFE ($m_{\mathrm{TFE}}=1.00$) and EtOH–TFE mixtures ($m_{\mathrm{ET}}=0.77$), fall on the aqueous alcohol line, while the point for acetic acid is below the aqueous acetone line. Obviously, the deviations from the mY correlation are inconsistent with the pattern anticipated for a contribution from the solvent nucleophilicity. This conclusion is brought to light in Fig. 2; in spite of the incorporation of the lN term for the solvent nucleophilicity, there is no significant improvement of the dispersal in Eq. 1. Indeed, the correlation analysis based on Eq. 1, which is given in Table 3, clearly indicates that the dispersion is not due to a contribution from solvent nucleophilicity to the overall process. The poor linearity ($R=0.96$; SD$=\pm0.33$) of the correlation with Eq. 1 is not significantly improved by including the best calculated (Fig. 2) but low nucleophilicity term of $l=0.06$. The dispersion observed for **1M** (Fig. 2) in the binary solvent mixtures series resembles that for **1H**. The precision of fit to Eq. 1 is still poorer than the precision level, $R=0.99$

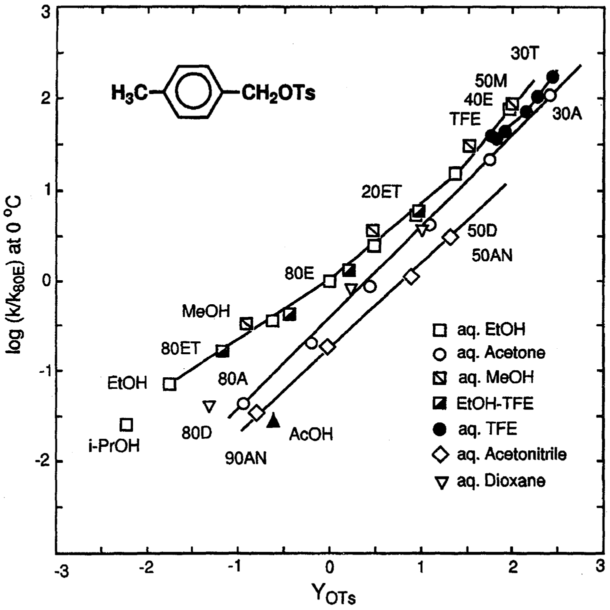

Fig. 1. The mY_{OTs} plot for solvolysis of p-methylbenzyl tosylate.

Table 1. Solvolysis Rates of *p*-Methylbenzyl Tosylate[a]

Solvent[b]	10^5k/s^{-1} 0 °C	10^5k/s^{-1} (Temp/°C)	$\Delta H^{\ddagger}_{0^\circ\mathrm{C}}$ [c] kcal mol^{-1}	$\Delta S^{\ddagger}_{0^\circ\mathrm{C}}$ [c] e.u.
40E	2330			
50E	472.8			
60E	162.4			
70E	74.34			
80E	30.53	543.9 (25)	18.1	−8.2
90E	10.71	195.7 (25)	18.3	−9.7
EtOH	2.138	46.63 (25)	19.4	−8.7
50M	2670			
60M	946.8			
80M	110.5	1766 (25),[d] 1469 (23.2)	17.4	−8.2
MeOH	10.14	197.0 (25)	18.7	−8.3
i-PrOH	0.7713			
30A	3310			
40A	672.7			
50A	124.6			
60A	26.00	485.2 (25)	18.4	−7.4
70A	6.145	128.3 (25)	19.1	−7.6
80A	1.299	29.10 (25)	19.6	−9.0
50D	114.8			
60D	24.84			
80D	1.21[d]	25.70 (25), 209.7 (45)	19.2	−10.4
50AN	84.96			
60AN	30.73			
80AN	5.363			
90AN	0.9789	18.02 (25)	18.3	−14.2
80ET	5.053			
60ET	12.93			
40ET	40.34			
20ET	181.4			
30T	5260			
40T	3200			
50T	2150			
80T	1340			
97Tw	1110			
TFE	1200			
AcOH	1.26[d,e]	21.8 (25),[e,f] 97 (40),[e]		
	0.833[d]	17.7 (25),[g] 19.60 (25),[h] 96.3 (40)[i]		

a) Conductimetrically determined, unless otherwise noted. b) Volume percent (v/v) of first-named organic component of mixed aqueous organic solvent, unless otherwise noted. Abbreviation, E=ethanol, M=methanol, A=acetone, D=dioxane, AN=acetonitrile, T=TFE=2,2,2-trifluoroethanol, and ET=ethanol–TFE mixtures (e.g., 80ET=80 : 20 (v/v) EtOH–TFE). Suffix w means weight percent (w/w). c) 1 cal=4.184 J and 1 e.u.=4.184 J K^{-1} mol^{-1}. d) Extrapolated from rate data at other temperatures. e) Ref. 14c. f) Estimated value from $k_{40^\circ\mathrm{C}}$. g) Titrimetrically determined. h) Conductimetrically determined; less reliable (Ref. 15b). i) Ref. 14d.

and SD=±0.1—0.15 of acceptable conformity.

The correlations based on Eq. 2 using various sets of Y_{Bz} scales appropriate for solvolysis of benzylic derivatives are summarized in Table 3. Both **1M** and **1S** do not correlate linearly with the Y_{OTs} parameter (Figs. 1 and 3), and the degree of fit of the correlation with alternative Y_{Bz} scales depends significantly upon the Y_{Bz} scale chosen. The *p*-methyl derivative **1M** still requires an appreciable contribution of the N_{OTs} term to give a satisfactory fit to Eq. 2. However, for **1S**, we obtained an excellent linear correlation against the neophyl **3H** Y_{neo} scale alone (R=0. 991; SD=±0.16), excluding the significant deviation of the point for AcOH. Consequently, the solvent effects on the solvolyses of **1S** and **1M** differ distinctly.

Discussion

Substituent Effects in Benzyl Tosylate Solvolysis. There is a gradual change in the solvolysis mechanism from $\mathrm{S_N1}$ to the conventional $\mathrm{S_N2}$ mechanism in the series of substituted benzyl tosylates as the substituent becomes more electron-withdrawing, and the solvent dependence of the ρ value should be a complementary probe of nucleophilic solvent assistance. Based on the solvolysis rates of benzyl tosylates **1M** and **1H**, we estimated two points ρ values vs. the Yukawa–Tsuno

Table 2. Solvolysis Rates of 3-Bromo-4-(methylthio)benzyl Tosylate[a)]

Solvent[b)]	$10^5k/\mathrm{s}^{-1}$ 0 °C	$10^5k/\mathrm{s}^{-1}$ (Temp/°C)	$\Delta H^{\ddagger}_{0\,°\mathrm{C}}$ [c)] kcal mol^{-1}	$\Delta S^{\ddagger}_{0\,°\mathrm{C}}$ [c)] e.u.
40E	8140			
50E	2130			
60E	893.0			
70E	369.1			
80E	147.4			
90E	44.04	810.9 (25)	18.3	−6.7
EtOH	5.799	129.0 (25)	19.5	−6.2
50M	13800[d)]	7580 (−5), 1085 (−20)	16.9	−0.3
60M	4572			
80M	549.5			
MeOH	34.38	683.1 (25)	18.8	−5.4
i-PrOH	2.237			
50A	576.5			
60A	124.2			
70A	28.23	545.8 (25)	18.6	−6.4
80A	6.081	130.2 (25)	19.3	−7.0
50D	411.4			
60D	79.85			
80D	3.31[d)]	12.16 (10), 72.73 (25)	19.5	−7.6
50AN	539.4			
60AN	209.5			
80AN	47.64			
90AN	10.15			
80ET	21.35			
60ET	95.81			
40ET	449.3			
20ET	2278			
50T	16500			
80T	12100[d)]	7140 (−5), 1300 (−20)	14.8	−8.5
97Tw	11500	7110 (−5), 1480 (−20)	13.6	−13.0
TFE	12200[d)]	7370 (−5), 1430 (−20)	14.2	−10.5
AcOH	4.477[e)]	100.1 (25)[f)]		

a)b)c)d) See footnotes a, b, c, and d of Table 1. e) Estimated value from the linear logarithmic rates plot between 25 and 0 °C. f) See footnote h of Table 1.

$\bar{\sigma}$-value at $r=1.3$ for the benzyl solvolysis[15)] in various solvents. Similar two-points ρ values for a more deactivating substituent were estimated from previous data for **1H** and *m*-chlorobenzyl tosylate **1C**.[1)] These ρ values (Table 4), which are the tangents of the curved Hammett plot at each substituent, range from −1.5 to −5.5 for the substituents investigated. The ρ values for limiting $\mathrm{S_N}1$ solvolysis of benzylic substrates are close to −5 in most solvents, except in aqueous TFE mixtures where a slightly higher value of −7 was found. As the magnitude of ρ is considered to reflect the charge developed at the benzylic α-carbon, the ρ values in Table 4 display a clear trend of increased charge with either an increase in Y or decrease in N value of the solvent. The tangent ρ values for the 3-bromo-4-methylthio substituted system seem to reach the limiting value ascribed to the $\mathrm{S_N}1$ solvolysis in essentially all the solvents. In contrast, nucleophilic solvent assistance is clearly seen as small $|\rho|$ values for the solvolysis of **1M** at least in the strongly nucleophilic solvents, e.g., EtOH, MeOH, and *i*-PrOH. The different dependence of the ρ value for **1S** and **1M** on the Y and N scales of the solvent is interpreted as due to a limiting $\mathrm{S_N}1$ mechanism for **1S** and a concerted $\mathrm{S_N}2$ mechanism with a varying transition state structure for **1M**.

Analysis of the Solvent Effect. In the analysis of the solvolysis of **1M** by the Winstein–Grunwald Eq. 1, an m value close to unity was found as expected for the limiting $\mathrm{S_N}1$ mechanism. This and the reduced l value compared with those observed for solvolyses of secondary alkyl systems (where the value was ascribed to nucleophilic solvation of a developing carbocation) suggest a large component of an ionization ($\mathrm{S_N}1$) process. However, the great dispersion between various binary aqueous solvent mixtures, coupled with the lack of downward deviations of the low- or non-nucleophilic solvents, indicates that Eq. 1 is incapable of describing precisely the solvent effect on the benzylic solvolysis. Nevertheless, there is a precise interrelation between the solvent effects of **1M** and **1H** (Eq. 3) indicating a little difference in the degree of involvement of solvent nucleophilicity,

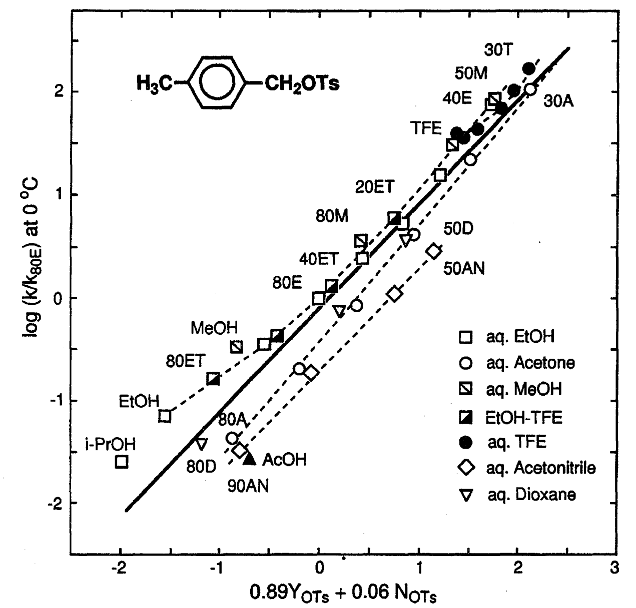

Fig. 2. The $(mY_{\mathrm{OTs}}+lN_{\mathrm{OTs}})$ plot for solvolysis of *p*-methylbenzyl tosylate.

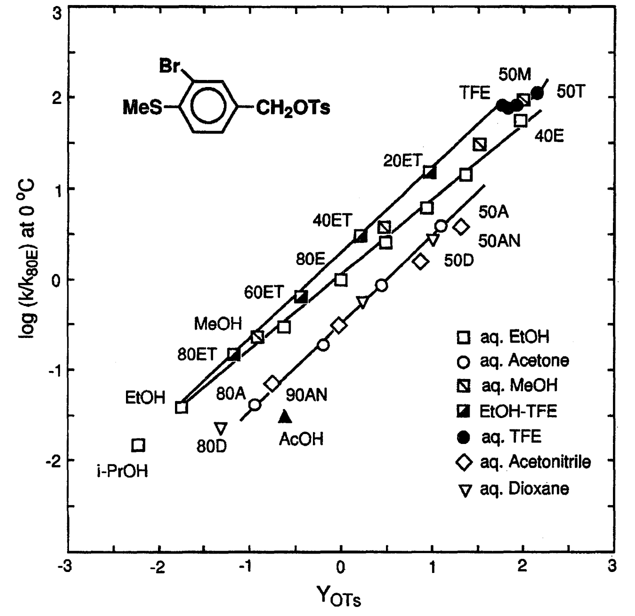

Fig. 3. The mY_{OTs} plot for solvolysis of 3-bromo-4-(methylthio)benzyl tosylate.

$$\log{(k/k_{80\mathrm{E}})_{1\mathrm{H}}}=0.72\ \log{(k/k_{80\mathrm{E}})_{1\mathrm{M}}}+0.36N_{\mathrm{OTs}}$$
$$(R{=}0.994 \text{ and } \mathrm{SD}=\pm 0.09). \qquad (3)$$

A similar interrelation but with different m and l values is found between **1S** and **1M**;

$$\log{(k/k_{80\mathrm{E}})_{1\mathrm{S}}}=1.04\ \log{(k/k_{80\mathrm{E}})_{1\mathrm{M}}}-0.14N_{\mathrm{OTs}}$$
$$(R{=}0.994 \text{ and } \mathrm{SD}=\pm 0.13). \qquad (4)$$

These correlations (Eqs. 3 and 4) suggest that common solvent polarity Y_{Bz} and common nucleophilicity N_{OTs} scales could account for the benzylic solvolysis. Indeed, the correlation of **1M** with Eq. 2 can be appreciably improved when either neophyl tosylate **3H** or α-(t-butyl)benzyl tosylate **2** are used as the reference substrates in place of 2-adamantyl tosylate, i.e., when Y_{neo} or $Y_{\alpha\text{-Bu}}$ is used as the Y_{Bz} scale in Eq. 2 (Table 3). This is not surprising because both the aryl-assisted and the benzylic $\mathrm{S_N}1$ solvolyses involve a similar degree of the aryl π-delocalization interaction mechanism of the incipient carbocation charge in the transition state, and most of the factors that cause the characteristic "dispersion behavior" of benzylic $\mathrm{S_N}1$ solvolysis can be accounted for on this basis.

An analysis based on Eq. 2 indicates that solvolysis of **1S** proceeds through an appreciably delocalized transition state within the limiting k_{c} mechanism, and the good correlation with the Y_{neo}–N_{OTs} treatment for **1M** indicates the involvement to a small extent ($l{\approx}0.2$) of solvent nucleophilicity. This may suggest a solvolysis through the $\mathrm{S_N}2$ (intermediate) mechanism[4,19] for **1M**, but not for **1S**.

The Y_{OTs} parameter reflects the solvent effect on an ionization leading to a localized 2-adamantyl carbocation. However, the dispersal is generally more significant for reactions involving highly delocalized carbocations.[6—12] An important reason for the dispersion of the mY_{OTs} plot for benzylic solvolyses is that the transition state for benzylic cation formation is effectively stabilized by the delocalization of the incipient cationic charge into the aryl ring. The resulting charge dispersal may be accompanied by a significant loss of the highly oriented solvent molecules at the reaction center, which differ for the different binary solvent mixtures.

We have proposed a new similarity comparison analysis of solvent effects (Eq. 5) for anchimerically assisted solvolyses.[20]

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

In this analysis, 2-adamantyl and p-methoxyneophyl (**3A**) tosylates model the k_{c} ($\mathrm{S_N}1$) and k_{Δ} mechanistic extremes, respectively, for the range of compounds undergoing neighboring group assistance. The adjustable blending parameters m_{c} and m_{Δ} show the extent to which any substrate approaches the unassisted 2-adamantyl ($m_{\Delta}{=}0$) or fully assisted p-methoxyneophyl ($m_{\mathrm{c}}{=}0$) in behavior.

We have demonstrated that a wide range of aryl-assisted k_{Δ} solvolyses with varying degrees of neighboring group assistance display successful LFER using the dual parameter Eq. 5 with the Y_{OTs} and Y_{Δ} parameters.[20] The M_{Δ} value defined by $0.51m_{\Delta}/(m_{\mathrm{c}}{+}0.51m_{\Delta})$[21] appears to monitor precisely the varying extent of aryl-bridging at the transition state of anchimerically assisted solvolyses. The extent of charge dispersal measured by M_{Δ} consistently changes on increasing the extent of aryl-assistance. The transition state for the aryl-assisted ionization is stabilized by π-delocalization ac-

Table 3. Correlation Analysis by Eq. 1 or Eq. 2[a)]

Y_{Bz}[b)]	m	l	c	R[c)]	SD[d)]	n[e)]
p-Methylbenzyl tosylate **1M**						
Y_{OTs}	0.89±0.05	0.06±0.08	−0.09	0.961	±0.33	35
$Y_{t\text{-Bu}}$	1.00±0.03	0.20±0.05	−0.12	0.984	±0.21	35
Y_{neo}	1.46±0.04	0.24±0.04	0.10	0.991	±0.16	35
Y_{Δ}	1.84±0.06	0.30±0.05	0.18	0.985	±0.20	35
3-Bromo-4-(methylthio)benzyl tosylate **1S**						
Y_{OTs}	0.93±0.05		−0.10	0.959	±0.33	31
	0.90±0.06	−0.11±0.08	−0.16	0.962	±0.33	31
$Y_{t\text{-Bu}}$	1.01±0.03		−0.20	0.989	±0.18	31
	1.02±0.03	0.03±0.05	−0.19	0.989	±0.18	31
Y_{neo}	1.42±0.04		−0.01	0.991	±0.16	31
	1.44±0.04	0.04±0.04	0.01	0.992	±0.16	31
Y_{Δ}	1.75±0.05		0.02	0.989	±0.18	31
	1.81±0.05	0.10±0.04	0.07	0.990	±0.16	31

a) Excluding the data in AcOH. b) $\log(k/k_{80\mathrm{E}}) = mY_{\mathrm{Bz}} + lN_{\mathrm{OTs}} + c$. $Y_{\alpha\text{-Bu}} = \log(k/k_{80\mathrm{E}})_{\alpha\text{-}(t\text{-Butyl})\mathrm{benzyl\ OTs}}$, $Y_{\mathrm{neo}} = \log(k/k_{80\mathrm{E}})_{\mathrm{Neophyl\ OTs}}$, and $Y_{\Delta} = \log(k/k_{80\mathrm{E}})_{p\text{-MeO-neophyl\ OTs}}$. c) Correlation coefficient. d) Standard deviation. e) Number of data points involved.

Table 4. Substituent Effects on the Solvolysis of Benzyl Tosylates at 25 °C[a)]

Solvent	ρ_{A}	ρ_{Me}	$\rho_{\mathrm{MeS,Br}}$	Y_{OTs}	N_{OTs}
80E	−2.4	−3.5	−4.99	0.00	0.00
EtOH	−2.0	−2.6	−3.16	−1.75	0.00
i-PrOH	−1.8	−2.4	−3.38	−2.23	−0.06
50M	−3.1		−5.18	2.00	−0.19
80M	−2.5	−3.7	−5.09	0.47	−0.05
MeOH	−2.2	−2.9	−3.88	−0.92	−0.04
80A	−2.0	−3.6	−4.89	−0.97	−0.42
50D	−3.1		−4.04	1.03	−0.29
80D	−2.2	−3.3	−3.22	−1.30	−0.29
50AN	−3.2		−5.85	1.31	−0.57
90AN	−2.1	−4.2	−7.37	−0.80	−1.24
30T	−4.2			2.43	−0.80
97Tw	−5.3	−7.0	−7.37	1.83	−2.79
20ET	−3.8		−8.03	0.98	−1.72
80ET	−2.2		−4.54	−1.18	−0.19
AcOH	−3.3	−5.0	−4.38	−0.61	−2.35
HCOOH	−5.3			3.04	−2.35

a) $\rho_{\mathrm{A}} = \log(k_{\mathrm{H}}/k_{m\text{-Cl}})/(-0.373)$, $\rho_{\mathrm{Me}} = \log(k_{p\text{-Me}}/k_{\mathrm{H}})/(-0.367)$, and $\rho_{\mathrm{MeS,Br}}$ (at 0 °C) $= \log(k_{4\text{-MeS-3-Br}}/k_{p\text{-Me}})/(-0.137)$ based on $r = 1.3$.

companied by the positive charge dispersal. Since the mechanism of charge delocalization by an aryl group is independent of whether the aryl group acquires it by anchimeric assistance or by being directly connected to the reaction center, the M_{Δ} scale should be also capable of correlating solvolysis reactions of various benzylic substrates. Thus, Eq. 5 had successfully correlated solvolysis reactions proceeding via transition states in which enhanced delocalization of the incipient carbocation charge takes place. The correlation results for relevant systems are summarized in Table 5.

Excellent correlations are of course obtained for aryl-assisted solvolyses; in particular, the solvolysis of neophyl tosylate **3H** — the reference Y_{Bz} in Eq. 2 — is precisely correlated by Eq. 5 with an M_{Δ} value of 0.75. The solvent effect on the solvolysis of **2** is likewise correlated and the $Y_{\alpha\text{-Bu}}$ parameter is characterized by an M_{Δ} value of 0.42. The solvolysis of **1S** was found now also to be satisfactorily correlated with Eq. 5 (Fig. 4).

Equation 5 may be rewritten in the form of Eq. 6,

$$\log(k/k_{80\mathrm{E}}) = \underline{m}[Y_{\mathrm{c}} + M_{\Delta}(\underline{Y}_{\Delta} - Y_{\mathrm{c}})], \tag{6}$$

where Y_{c} is the ionizing power scale for the nondelocal-

Table 5. Correlation Analysis of Solvent Effects on Solvolyses:[a] $\log(k/k_{80E}) = m_c Y_{OTs} + m_\Delta Y_\Delta + lN_{OTs}$

No.	R in ROTs	°C	m_c	m_Δ	l	M_Δ[b]	$\underline{m}$[c]	R[d]	SD[e]	n[f]
1.	p-Methoxyneophyl	45	0.00	1.00		1.00	0.51	(Definition)		
2.	Neophyl	45	0.16	0.95		0.75	0.64	0.998	±0.06	45
3.	α-(t-Butyl)benzyl	25	0.55	0.79		0.42	0.95	0.995	±0.15	41
			0.57	0.75	−0.02	0.40	0.95	0.995	±0.15	41
4.	α-(t-Butyl)-m-chlorobenzyl	25	0.57	0.68		0.38	0.92	0.994	±0.14	31
			0.56	0.71	0.02	0.39	0.92	0.994	±0.14	31
5.	α-CF_3-α-Me-benzyl	45	0.70	0.40		0.23	0.90	0.991	±0.16	38
			0.60	0.71	0.15	0.38	0.96	0.996	±0.12	38
6.	α-CF_3-α,p-Me_2-benzyl	45	0.58	0.89		0.44	1.03	0.995	±0.12	29
			0.60	0.86	−0.02	0.42	1.03	0.995	±0.12	29
7.	α-CF_3-p-MeO-benzyl	45	0.30	0.87		0.60	0.74	0.995	±0.10	33
			0.31	0.84	−0.02	0.58	0.73	0.995	±0.10	33
8.	α-CF_3-p-Me-benzyl	45	0.80	0.29		0.16	0.95	0.994	±0.13	26
			0.62	0.76	0.15	0.38	1.00	0.998	±0.07	26
9.	1-(m-Cl-phenyl)ethyl	25	0.55	0.65	0.36	0.37	0.88	0.993	±0.13	32
10.	1-(p-NO_2-phenyl)ethyl	25	0.57	0.32	0.74	0.22	0.73	0.988	±0.16	33
			0.59	0.28	0.88	0.19	0.73	0.993	±0.12	32[g]
11.	3-Bromo-4-(methylthio)benzyl	0	0.28	1.28		0.70	0.93	0.994	±0.13	31
			0.26	1.35	0.06	0.72	0.94	0.995	±0.12	31
12.	p-Methylbenzyl	0	0.38	1.01		0.58	0.90	0.981	±0.23	35
			0.28	1.32	0.25	0.70	0.94	0.991	±0.17	35
13.	m-Methylbenzyl	25	0.16	1.25	0.50	0.80	0.79	0.991	±0.13	37[h]
14.	Benzyl	25	0.18	1.12	0.58	0.76	0.74	0.991	±0.13	38[h]
15.	m-Chlorobenzyl	25	0.10	0.91	0.80	0.82	0.56	0.985	±0.14	38[h]
16.	p-Nitrobenzyl	25	0.20	0.42	1.00	0.51	0.41	0.991	±0.10	35
17.	2-Adamantyl	25	1.00	0.00		0.00	1.00	(Definition)		

a) Excluding data of AcOH. b) $M_\Delta = 0.51m_\Delta/(m_c + 0.51m_\Delta)$. c) $\underline{m} = m_c + 0.51m_\Delta$. d) Correlation coefficient. e) Standard deviation. f) Number of data points involved. g) Excluding data of 97Tw. h) Excluding data of MeOH, EtOH, i-PrOH, and 97% HFIP.

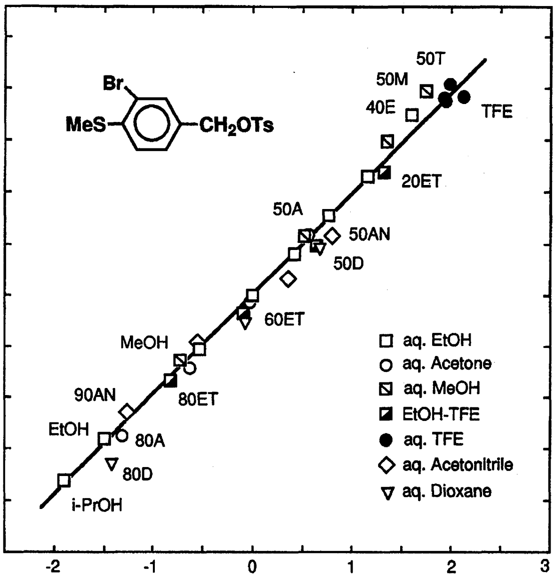

Fig. 4. The $(m_c Y_{OTs} + m_\Delta Y_\Delta)$ plot for solvolysis of 3-bromo-4-(methylthio)benzyl tosylate.

ized transition state referable to Y_{OTs}, and $\underline{Y}_\Delta$ is that for the delocalized transition state referred to the normalized Y_Δ scale by a factor of 1/0.51.[21] The susceptibility parameter $\underline{m}$ corresponds to $m_c + 0.51m_\Delta$ and the coefficient M_Δ corresponds to $0.51m_\Delta/(m_c + 0.51m_\Delta)$ in Eq. 5. We have used in Eq. 6 the same framework of charge-localization and delocalization components by the solvent as we had done in the Yukawa–Tsuno framework for the substituent effect.[17] The M_Δ value parallels the resonance demand parameter r in the Yukawa–Tsuno Equation (Eq. 7),[17]

$$\log(k/k_o) = \rho[\sigma^\circ + r(\sigma^+ - \sigma^\circ)], \tag{7}$$

and it is a generalized scale capable of diagnosing the degree of charge delocalization (including the delocalization of aryl-bridging) in the transition state. Thus, Y_{neo} with $M_\Delta = 0.75$ and $Y_{\alpha\text{-Bu}}$ with $M_\Delta = 0.42$ are placed on a single M_Δ scale with the points $M_\Delta = 1.00$ for the p-methoxyneophyl Y_Δ and $M_\Delta = 0.00$ for the 2-adamantyl Y_{OTs}. This unified treatment removes the proliferation in the appropriate Y_{Bz} references required for the simple similarity comparison analysis (Eq. 2). The M_Δ value of 0.70 for **1S** is close to the value for **3H** in line with the fact that the best Y_{Bz} function for correlative purposes (Table 3) is Y_{neo}. An interesting example is the solvolysis of tris(p-methoxyphenyl)vinyl tosylate, for which the extremely high M_Δ value of 1.56 indicates highly enhanced delocalization by the p-methoxyphenyl group on the α-position forming a transition state.[12] A wide range of benzylic chloride solvolyses, including p-methoxybenzyl, 1-(substituted phenyl)ethyl, α-cumyl, and benzhydryl chlorides, have been correlated successfully with equations similar to Eq. 5.[6b)] Unfortunately, due to the high solvolytic reactivities of benzyl tosylates, the available tosylate solvolysis data are limited to systems leading to strongly destabilized carbocations. Hence, for most of them, a significant contribution of solvent nucleophilicity must be taken into account by correlation with the multi-parameter Eq. 8.

$$\log{(k/k_{80\mathrm{E}})} = m_{\mathrm{c}} Y_{\mathrm{OTs}} + m_{\Delta} Y_{\Delta} + lN. \qquad (8)$$

Thus Eq. 8 rather than Eq. 5 has been used to correlate the solvolysis data for **1M** and derivatives carrying electron-withdrawing substituents, and for other relevant deactivated benzylic precursors (Table 5). Obviously, Eq. 8 can be successfully applied to benzylic solvolyses ranging widely from typical $\mathrm{S_N}1$ to $\mathrm{S_N}2$ mechanisms. For many of them we find excellent correlations with none or only small involvement of the nucleophilicity. This strongly suggests that Eqs. 5 and 6 are generally applicable to tosylate solvolyses proceeding through the $\mathrm{S_N}1$ mechanism. For example, the behavior of **1S** differs from that of the slightly less deactivated **1M**. The m value decreases significantly and the l value increases rapidly in parallel as the substituent becomes more electron-withdrawing. The strong cation-stabilizing effect of the 3-bromo-4-(methylthio)phenyl group appears a necessary condition for the solvolysis of **1S** proceeding by a limiting $\mathrm{S_N}1$ mechanism in all the solvents.[16b)] Less activated substrates react by a nucleophilically assisted, $\mathrm{S_N}2$ and/or $\mathrm{S_N}2$ (intermediate) mechanism. A very significant feature is that despite the significant involvement of solvent nucleophilicity, all the derivatives, including strongly electron-withdrawing ones, display a high M_{Δ} value of about 0.7, which is expected only for processes generating an appreciable positive charge. This behavior contrasts sharply with that of the 1-phenylethyl solvolysis,[22)] where the m-chloro and p-nitro derivatives gave a low M_{Δ} of 0.2—0.4 and an $\underline{m}$ as high as 0.8. As measured by M_{Δ}, the extended delocalization is much more important in the primary benzylic than in the secondary benzylic systems, regardless of whether the $\mathrm{S_N}1$ or $\mathrm{S_N}2$ mechanism is operating.

Mechanisms of Benzylic Solvolysis. This analysis of the Winstein–Grunwald Equation leads to the conclusion that the solvolysis of tosylates **1M** and **1H** shows an intermediate response both to the solvent polarity Y and to the solvent nucleophilicity N. The correlation with both the enhanced polarity and nucleophilicity terms suggests a single-step concerted displacement mechanism with a high incipient cationic charge in the solvolysis. It is difficult to fit such solvent effects into the classical $\mathrm{S_N}1$ vs. $\mathrm{S_N}2$ division, and a spectrum of transition states between those for the pure $\mathrm{S_N}1$ and $\mathrm{S_N}2$ mechanisms, and possibly involving the "$\mathrm{S_N}2$ (intermediate)" mechanism seems more likely. By the term "$\mathrm{S_N}2$ (intermediate)", Bentley and Schleyer emphasized the possibility that an $\mathrm{S_N}2$ reaction may proceed via a nucleophilically solvated (ion pair) intermediate.[4,19)] Its rate-determining transition state may involve a late transition state (i.e., a transition state close to the intermediate) for a bimolecular displacement with a high carbocationic character in a continuous spectrum of $\mathrm{S_N}2$ mechanisms. In contrast, the borderline solvolysis where the classical $\mathrm{S_N}1$ and $\mathrm{S_N}2$ mechanisms are simultaneously operative can not be exactly described by the mY and lN terms of Eq. 1; its rate should be given by a sum of the rate constants for independent $\mathrm{S_N}1$ and $\mathrm{S_N}2$ processes. Good linear interrelations (Eqs. 3 and 4) among substituted benzylic derivatives displaying varying contributions of solvent nucleophilicity may argue for a common concerted $\mathrm{S_N}2$ displacement mechanism, but are inconsistent with the simultaneous operation of simple classical $\mathrm{S_N}2$ and $\mathrm{S_N}1$ mechanisms in the borderline region. Nevertheless, Richard and Jencks have argued for the latter blend of processes for the benzylic solvolysis, based on product selectivity analysis.[23)] Likewise, Kevill prefers, but without supporting evidence, the superimposition of $\mathrm{S_N}1$ and $\mathrm{S_N}2$ mechanisms over the intermediate mechanism.[24)]

We have recently observed a significant internal return in the solvolysis of **1S** and **1M** in most solvents, and even varying extents of internal return in the solvolysis of the parent **1H** in the lower nucleophilicity solvents but none in nucleophilic solvents.[16)] The existence of ion pair return is the most convincing evidence against the operation of any single-step mechanism proceeding without an intermediate through an essentially nondissociative rate-determining transition state. Hence, the $\mathrm{S_N}2$ (intermediate) mechanism seems highly likely for the moderately solvent-assisted solvolysis of benzyl tosylates **1M** and **1H**. However, if this mechanism occurs without internal return as assumed by Schleyer, Bentley, and co-workers,[4,19)] the benzylic solvolyses must proceed through a parallel $\mathrm{S_N}2$ [or $\mathrm{S_N}2$ (intermediate)] mechanism and a classical $\mathrm{S_N}1$ mechanism involving significant internal return. There is no particular reason to assume the absence of return from the "$\mathrm{S_N}2$ (intermediate)" process. Indeed, the Jencks–Richard preassociation mechanism may involve a preequilibrium ionization step of the nucleophilically solvent-associated precursor,[25)] which should be equivalent to the $\mathrm{S_N}2$ (intermediate) mechanism, as far as the structure of the transition state species is concerned. The simplest assignment is a classical $\mathrm{S_N}1$ mechanism for **1S** and an $\mathrm{S_N}2$ (intermediate) mechanism involving appreciable return for **1M**. The transition state for the latter reaction involves a small extent of solvent nucleophilicity ($l \approx 0.1$ in Eq. 1) so that the transition state in any less nucleophilic solvent should be essentially indiscernible from the limiting $\mathrm{S_N}1$ transition state. The deviations of highly nucleophilic EtOH, MeOH, and *i*-PrOH from the *mY*–*lN* correlation for **1M** and **1H** may be attributed to a decreased internal return due to effective capture at the ion pair stage of the S_N2 (intermediate) process by the strongly nucleophilic solvent. Even though the deviation might be rationalized by a competition of this extended S_N2 and classical S_N1 mechanisms as well as by a single S_N2 (intermediate) mechanism, the extent of deviation from Eq. 8 in the solvolysis leading to a rather stable cation is too small and is observable only in a few solvents to warrant interpretation. To identify the nature of the transition state or of the ion pair, it seems necessary to examine in further detail the salt effects in these solvolyses.

On the other hand, we often encounter cases where S_N2 solvolyses have a nonlinear response to the conventional N_{OTs} scale based on MeOTs solvolysis.[26] Indeed, only by a precise evaluation of the dependence on Y can we gather sufficient information to enable us to discuss in detail the nature of the involvement of solvent nucleophilicity. The degree of the solvent assistance may vary as a nonlinear (quadratic) function of the solvent nucleophilicity, implying an enhanced mechanistic shift in stronger nucleophilic solvents.[26] There is still considerable doubt whether the linearity of $\log k$ with solvent nucleophilicity holds over a wide range of substituted benzyl series. Further examination of the solvent nucleophilicity term in the solvolysis of strongly deactivated benzyl tosylates, where it should play a more important role, is required.

Experimental

Materials: Benzyl tosylates were prepared by the Schotten–Bauman method,[14d] as described earlier:[1,2,15a] The *p*-methyl derivative **1M**, was recrystallized from ether–petroleum ether, mp 49—51 °C (decomp), lit,[27] mp 57.9—58.5, 49.5—50.5 °C.[14c] Anal. Found: C, 64.99; H, 5.98%. Calcd for $C_{15}H_{16}O_3S$: C, 65.19; H, 5.84%. The 3-bromo-4-methylthio derivative **1S**, mp 80.0—84.5 °C, was recrystallized from benzene–petroleum ether. Anal. Found: C, 46.70; H, 3.96%. Calcd for $C_{15}H_{15}O_3S_2Br$: C, 46.52; H, 3.90%.

Organic solvents and water were purified as described earlier.[1,2,6,10,11,26,28] The binary solvent mixtures were prepared by mixing the corresponding volumes or weights of the 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 the appropriate temperature, which was controlled within ±0.01 °C.[1,2] The acetolysis rates were measured by the ordinary titrimetric method[28] and also by the conductimetric method.[15b]

The experimental errors in the rate constants calculated from the conductivity runs were generally less than 1.0%. The titrimetrically measured rate constants were slightly less accurate but were nevertheless reproducible within ±1.5% in repetitive runs.

This work was partially supported by Grants-in-Aid for Scientific Research Nos. 02640398, 02403010, 05453032, and 06453041 from the Ministry of Education, Science and Culture.

References

1) M. Fujio, T. Susuki, Y. Tsuji, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **18(2)**, 243 (1992); M. Fujio, T. Susuki, M. Goto, Y. Tsuji, K. Yatsugi, Y. Saeki, S. H. Kim, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **67**, 2233 (1994).

2) M. Fujio, T. Susuki, K. Yatsugi, Y. Saeki, G. A.-W. Ahmed, Y. Tsuji, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **18(2)**, 257 (1992); M. Fujio, T. Susuki, M. Goto, Y. Tsuji, K. Yatsugi, S. H. Kim, G. A.-W. Ahmed, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **68**, 673 (1995).

3) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948); A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956); A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **79**, 1597 and 1602 (1957); A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **79**, 1608 (1957); S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957).

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

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

6) a) S. Usui, Y. Shibuya, T. Adachi, M. Fujio, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **14(2)**, 355 (1984); b) K. Nakata, H. Nomura, H. Nakamura, S. Usui, Y. Tsuji, I. Akasaka, M. Fujio, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **18(2)**, 297 (1992).

7) 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); K.-T. Liu, J.-S. Yang, S.-M. Chang, Y.-S. Lin, H.-C. Sheu, and M.-L. Tsao, *J. Org. Chem.*, **57**, 3041 (1992); K.-T. Liu, H.-Y. Hsu, and J.-S. Yang, *Tetrahedron Lett.*, **33**, 3327 (1992); K.-T. Liu and H.-C. Sheu, *J. Phys. Org. Chem.*, **6**, 122 (1993); K.-T. Liu, H.-I. Chen, and C.-P. Chin, *J. Phys. Org. Chem.*, **4**, 463 (1991); K.-T. Liu, L.-W. Chang, and P.-S. Chen, *J. Org. Chem.*, **57**, 4791 (1992).

8) T. W. Bentley, I. S. Koo, and S. J. Norman, *J. Org. Chem.*, **56**, 1604 (1991); T. W. Bentley, J.-P. Dan-Schmidt, G. Llewellyn, and H. Mayr, *J. Org. Chem.*, **57**, 2387 (1992); T. W. Bentley, M. Christl, R. Kemmer, G. Llewellyn, and J. E. Oakley, *J. Chem. Soc., Perkin Trans. 2*, **1994**, 2531.

9) D. N. Kevill and M. J. D'Souza, *J. Phys. Org. Chem.*, **5**, 287 (1992); D. N. Kevill, N. H. Ismail, and M. J. D'Souza, *J. Org. Chem.*, **59**, 6303 (1994).

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) M. Fujio, M. Goto, K. Funatsu, T. Yoshino, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **17(2)**, 255 (1990); M. Fujio, M. Goto, K. Funatsu, T. Yoshino, Y. Saeki, K. Yatsugi, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **65**, 46 (1992).

12) M. Fujio, M. Goto, Y. Tsuno, S. Kobayashi, and H. Taniguchi, *Tetrahedron Lett.*, **31**, 7039 (1990); M. Fujio, N. Tomita, Y. Tsuno, S. Kobayashi, H. Taniguchi, J. Kaspi, and Z. Rappoport, *Tetrahedron Lett.*, **33**, 1309 (1992).

13) Y. Tsuji, M. Fujio, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **17(2)**, 281 (1990); *Tetrahedron Lett.*, **33**, 349 (1992).

14) a) G. S. Hammond, C. E. Reeder, F. T. Fang, and J. K. Kochi, *J. Am. Chem. Soc.*, **80**, 568 (1958); b) Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957); c) Y. Okamoto and H. C. Brown, *J. Am. Chem. Soc.*, **89**, 370 (1967); d) A. Streitwieser, Jr., H. A. Hammond, R. H. Jagow, R. M. Williams, R. G. Jesaitis, C. J. Chang, and R. Wolf, *J. Am. Chem. Soc.*, **92**, 5141 (1970); e) P. R. Young and W. P. Jencks, *J. Am. Chem. Soc.*, **101**, 3288 (1979); J. M. Harris, D. L. Mount, M. R. Smith, W. C. Neal, Jr., M. D. Dukes, and D. J. Raber, *J. Am. Chem. Soc.*, **100**, 8147 (1978); J. M. Harris, S. G. Shafer, J. R. Moffatt, and A. R. Becker, *J. Am. Chem. Soc.*, **101**, 3295 (1979).

15) a) M. Fujio, M. Goto, T. Susuki, M. Mishima, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **63**, 1146 (1990); b) M. Fujio, M. Goto, T. Susuki, M. Mishima, and Y. Tsuno, *J. Phys. Org. Chem.*, **3**, 449 (1990); c) M. Fujio, I. Akasaka, S. H. Kim, M. Mishima, Y. Tsuji, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **18(1)**, 131 (1991).

16) a) M. Fujio, F. Sanematsu, Y. Tsuno, M. Sawada, and Y. Takai, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **16(2)**, 193 (1988); Y. Tsuji, F. Samenatsu, Y. Saeki, K. Yatsugi, M. Fujio, Y. Tsuno, M. Sawada, and Y. Takai, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **18(2)**, 267 (1992); b) Y. Tsuji, S. H. Kim, Y. Saeki, K. Yatsugi, M. Fujio, and Y. Tsuno, *Tetrahedron Lett.*, **36**, 1465 (1995).

17) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **32**, 971 (1959); Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jpn.*, **39**, 2274 (1966).

18) D. N. Kevill and T. J. Rissmann, *J. Chem. Soc., Perkin Trans. 2*, **1984**, 717; D. N. Kevill and T. J. Rissmann, *J. Chem. Res. Synop.*, **1986**, 252; D. N. Kevill and H. Ren, *J. Org. Chem.*, **54**, 5654 (1989).

19) T. W. Bentley, C. T. Bowen, D. H. Morten, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **103**, 5466 (1981); T. W. Bentley and G. E. Carter, *J. Am. Chem. Soc.*, **104**, 5741 (1982).

20) Presented at "5th Kyushu International Symposium on Physical Organic Chemistry," in Fukuoka, October 1993, Abstr., p. 84; at "36th Korean Association of Physical Organic Chemists," in Seoul, July 1994, Abstr., p. 13; and at "IUPAC 12th Conference on Physical Organic Chemistry," in Padova, August 1994, Abstr., p. 93; Y. Saeki, Ph. D. Thesis, Kyushu University, October 1994; M. Fujio, Y. Saeki, K. Nakamoto, K. Yatsugi, N. Goto, S. H. Kim, Y. Tsuji, Z. Rappoport, and Y. Tsuno, *Bull. Chem. Soc. Jpn.*, **68**, 2603 (1995).

21) The average susceptibility m values obtained by applying the Y_{Δ} scale are found to be equivalent to twice of the corresponding Winstein–Grunwald m values against Y_{OTs} for all the substrates studied. For a reasonable similarity comparison, both Y_{Δ} and Y_{OTs} parameters should have equivalent susceptibilities. In order to measure properly the degree of anchimeric assistance effect on these aryl-assisted solvolyses, it seems necessary to normalize the m_{Δ} scale, especially when we define the parameter for the charge-delocalization effect $\underline{Y}_{\Delta}-Y_{\mathrm{OTs}}$. The solvent effects in aqueous acetone mixtures in all the cases gave excellent linear correlations ($R>0.998$) against both Y_{OTs} and Y_{Δ} regardless of mechanisms. The ratios of m values derived from plots against Y_{OTs} vs. plots against Y_{Δ} have a constant value of 0.51 for more than 60 solvolyses of varying mechanisms. This led to a definition of a conventional measure $\underline{m}$ of the response to the solvent polarity as $\underline{m}=(m_{\mathrm{c}}+0.51m_{\Delta})$; the degree of aryl-assistance is then $0.51m_{\Delta}/(m_{\mathrm{c}}+0.51m_{\Delta})$ for any given substrate.

22) Unpublished results from this laboratory.

23) J. P. Richard and W. P. Jencks, *J. Am. Chem. Soc.*, **106**, 1373 (1984).

24) D. N. Kevill and G. M. L. Lin, *J. Am. Chem. Soc.*, **101**, 3916 (1979).

25) W. P. Jencks, *Acc. Chem. Res.*, **6**, 161 (1980).

26) G. A.-W. Ahmed, K. Yatsugi, Y. Saeki, M. Goto, Y. Tsuji, S. Ouchi, M. Fujio, and Y. Tsuno, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **19(1)**, 63 (1993).

27) J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, **75**, 3443 (1953).

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